

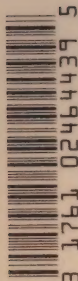
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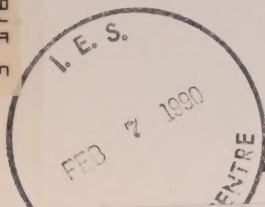
AN ASSESSMENT OF THE EFFECT OF HALONS ON THE ENVIRONMENT

/ Forester, A.J.; McConnell, J.C.; Evans, W.F.J. 1989.



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A.J. Forester, J.C. McConnell and W.F.J. Evans

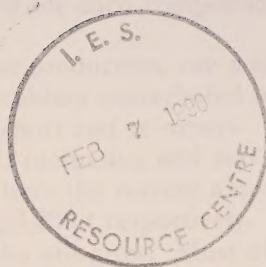
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December 1989

An Assessment Of The Effect Of Halons On The Environment

**A.J. Forester, J.C. McConnell
and W.F.J. Evans**



**Atmospheric Research Directorate
ARD 89-007**

DECEMBER 1989



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Summary

Halons are halogenated organic compounds widely and increasingly used as fire suppressants and specialised refrigerants. They are chemically similar to chlorofluorocarbons (CFCs) except that they contain one or more bromine atoms in the molecule and may not contain chlorine. They are chemically stable with a long atmospheric lifetimes and their release of bromine on photolysis ensures that they are potent destroyers of ozone on reaching the stratosphere. Halons also function as greenhouse or radiatively active gases (RAGs) gases and so are potential contributors to an anthropogenic climatic warming.

This report briefly reviews the formation of ozone in the stratosphere and the manner in which it is destroyed by man-made organic compounds with emphasis on the ozone-depleting properties of bromine species (Br_x) such as are liberated on the photolysis of halons. The current status of knowledge on the production, use, emissions and environmental impact of halons is also appraised.

There are two principal halons: halon 1211 used primarily in small portable fire extinguishers and 1301 employed in total flooding of large, fixed installations (e.g., computer rooms, petrochemical plant etc.). Halon 2402 is not widely used in fire control but has some specialised military applications. The *Characteristics; Development Production and Use; Banks and Emission to the Atmosphere; Atmospheric Sinks; Atmospheric Lifetime; Ozone Depletion Potential and Future Scenarios* are reviewed for each compound where such information is available.

Information on the production, use and emission of halons to the atmosphere is not very reliable, a problem exacerbated by the global trade in halons with a complex pattern of export and re-export. Yearly global production of halons 1211 and 1301 varies but is increasing and may be as high as 13,000 t and 8,000 t y^{-1} respectively. In addition, the current amounts banked in fire control systems may exceed 17,000 t and 25,000 t respectively. Even if production were to be cut back, the size of these banks will grow. Most of the halon emission to the atmosphere results from inadvertent releases and testing, with only ~25% from fire control. Current tropospheric abundances are <2 pptv but halon 1211 is increasing at ~12% and halon 1301 at 4-5% annually. The abundance of both decreases markedly in the stratosphere. Both halon 1211 and 1301 have long atmospheric lifetimes (~25 y and 80-110 y respectively) and significant ozone depletion potentials (~2.7, ~11.0; halon 2402, ~6.0)

A number of numerical simulations have predicted a dramatic increase in halon production and the size of the 'banks but only two of the most recent studies have examined scenarios in which halon production is pegged at the 1986 level by 1992 as required under the *Montreal Protocol*. These both suggest that much stricter controls will be required to ameliorate the effects of halons on the ozone layer. Their role in climate warming is confirmed although their contribution will probably not be large.

These simulations need to be critically appraised with respect to their performance (sensitivity analyses etc.) and should be used to examine a greater range of scenarios relating to the fate of the halon bank.

All aspects of the chemistry and dynamics of environmentally persistent bromine compounds in the atmosphere require closer scrutiny, particularly the detection of Br species in the troposphere and stratosphere and clarification of Br/Cl catalytic cycles. Compared with the attention given to Cl, Br compounds (natural and man-made) are not adequately monitored.

Industrial associations have recognised the environmental problems created by halons and examined operational protocols to identify sources of unwanted emission. It is not clear how generally their recommendations have been adopted. No environmentally benign substitutes for halons are expected to be available for 5-10 years. Management of the large and growing halon bank therefor emerges as a problem at least as important as the need to control production. This requires further study and probably legislation to ensure that the banked halons are disposed of and/or recycled and the environmental impacts are minimised.

The halons 1211, 1301 and 2402 are harmful to the environment and may warrant inclusion on the *Priority Substances List* of the *Canadian Environmental Protection Act*.

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Scope, Terms of Reference

Halons 1211, 1301 and 2402 were included under the *Montreal Protocol* and are on Environment Canada's list of substances nominated as potentially toxic. They are not currently included on the *Priority Substances List (PSL)* or under *Schedule 1* of the *List of Toxic Substances (LTS)* designated by the *Canadian Environmental Protection Act (CEPA)*.

This report briefly reviews the formation of stratospheric ozone and the mechanisms by which it is destroyed by active halogen species, notably bromine, liberated on the breakdown of man-made pollutants. The *Characteristics; Development, Production and Use; Banks and Emission to the Atmosphere; Atmospheric Sinks; Atmospheric Lifetime; Ozone Depletion Potential* and *Future Scenarios* are reviewed where such information is available. The role of halons in climatic warming (i.e., the so-called *greenhouse* warming) is also considered.

The possibility of controlling bromine releases from halons is assessed with respect to operational considerations, the use of alternatives, recycling programmes and their phase down and complete proscription.

Acknowledgements

Mr G. Taylor of Taylor/Wagner Inc., Dr M. McFarlane of E.I. DuPont de Nemours & Co. (DuPont) and Mr J. Ziemba of the Halon Research Institute (HRI) were of great assistance with respect to current information on halon production and use and provided many useful comments on halons from the industry perspective.

The *Shaping Options for Ozone Protection* meeting, organised by the Friends of the Earth (FOE) and Environment Canada, held in Toronto on the 30th November 1988, provided a timely opportunity to review the current status of developments in research on stratospheric ozone; the production, use, control and development of alternatives for a number of ozone depleting chemicals (including halons) and national and international responses following the *Montreal Protocol (MP)* and World Climate Conferences in Toronto and the Hague. The meeting provided opportunities for informal discussions with people from industry, non-governmental organisations (NGOs) and government. In this regard discussions with Drs G.V. Buxton and T. Leah (Environment Canada) and Dr A.D. FitzGerald (Northern Telecom Ltd.) were of particular value.

The numerical simulation on the stratospheric impact of halons¹ was undertaken with Drs G.S. Henderson of the Atmospheric Environment Service, Environment Canada (AES), now of the University of Toronto, and Ms E.M.J. Templeton of (York University) will be the subject of separate publications currently in preparation.

Dr J. Reid of the AES provided valuable background information on the context of the *Canadian Environmental Protection Act (CEPA)* and Dr D.I. Wardle (AES) gave valued technical and editorial advice on all aspects of the document and facilitated its production as an Atmospheric Research Directorate publication. Mr B. Kuntz (AES) undertook a number of technical literature searches in support of the work.

¹ This work was supported by contract to Dr J.C. McConnell from the AES (DSS File No. 07SE.KM172-8-7447).

contract² from the AES and Department of Supply and Services, DSS), who thanks Mr E. Pecile and Ms L. Stadelbauer of the DSS and Mr R. Hoogerbrug of the AES for their assistance and cooperation.

² Serial No KM172-8-7286/01-SE; File No 07SE.KM172-8-7286

Introduction³

Ozone is an important atmospheric trace gas influencing the radiative transfer, dynamics and chemistry of the stratosphere and ultimately the troposphere, climate, and biosphere.

As the major gas within the atmosphere responsible for absorbing solar ultraviolet (UV) or shortwave radiation in the 200-330 nm region, ozone protects both plant and animal life from the harmful effects of this radiation, particularly in the biologically active UV-B (280-315 nm) part of the spectrum. The intensity of UV radiation at any particular location near the ground depends primarily upon the total number of ozone molecules distributed throughout the atmosphere directly above that point (the column ozone or simply total ozone). In addition, by absorbing solar radiation, the ozone layer is the principal heat source within the middle atmosphere. It is therefore primarily responsible for generating the inversion that characterizes the stratosphere which establishes the tropopause separating the stratosphere from the lower atmosphere or troposphere. The existence of the ozone layer, with its special properties of radiation transfer, is then a primary determinant of the structure and behaviour of the normal atmosphere. Any significant and long-term decrease in the concentration of ozone within the atmosphere will influence the atmospheric stability, global circulation and climate, UV flux to the surface and will have a detrimental effect upon life on the planet.

For example, it is argued that significant depletion of stratospheric ozone could cause an enhancement of UV radiation at the earth's surface, increasing human morbidity and mortality through carcinogenic and immunosuppressive effects. Some other biota would also suffer such effects and the phytotoxic action of UV-B could adversely affect the primary producers of most ecosystems with a cascade effect propagating through the trophic levels of the food chain, adversely affecting terrestrial and aquatic systems including fisheries, forests and agriculture.

³ This text taken in part from Evans, Fast, Forester, Henderson, Kerr, Vupputuri & Wardle (1987).

Other trace gases, the Radiatively Active Gases (RAGs) or greenhouse gases, absorb the outgoing terrestrial longwave, infrared radiation contributing to the anthropogenic enhancement of the natural (so-called) greenhouse or blanket effect.

The 1987 global column reduction of ozone caused by increasing levels of chlorofluorocarbons (CFCs) in the atmosphere was calculated to be of the order of 1 per cent. Given the current accuracy of the global data⁴ such a reduction is difficult to assess and has perhaps led to a lack of awareness of the potential seriousness of the problem. However, the discovery of an Antarctic ozone hole (Farman *et al.*, 1985a,b) has renewed concern over the influence of anthropogenic emissions on stratospheric ozone and emphasizes how poorly understood are the mechanisms responsible for the integrity of the ozone layer. The problem is now compounded by the existence of an ozone depletion in the Arctic which is also *prima facie* partly the result of anthropogenic emissions although the relative importance of chemical and dynamical processes appear to differ from its S. hemisphere counterpart.

In reviewing the trace substances that catalytically control stratospheric ozone, the WMO group included "to a lesser extent BrO_x species" (WMO, 1985:2). The WMO panel concluded and recommended that "Uncertainties in the data base for BrO_x and coupled BrO_x-ClO_x catalysed ozone destruction need to be reduced" (WMO, 1985:6). These uncertainties are also underlined by Singh *et al.* (1988:594, citing Penkett *et al.*, 1985; the WMO, 1985: 636,637 & 643; Fabian, 1986 and Cicerone *et al.*, 1988) who draw attention to the paucity and preliminary nature of the data on BrO_x species in the middle atmosphere. There has been growing evidence that the atmospheric concentration of gases which are a source of stratospheric bromine may be changing as a result of human activity (WMO, 1985:2). The urgency is evident considering "chlorine and bromine abundances are currently thought to be the primary determinants of the risk of ozone depletion"⁵ (Hoffman & Gibbs, 1988:4).

⁴ For a critical appraisal of the global ozone monitoring systems see Evans *et al.*, 1987).

⁵ Emphasis in the original.

Bromoform, primarily natural in origin, and methyl bromide (about half originating from natural, mostly marine, sources and half from human activity) dominate the brominated compounds in the atmosphere (WMO, 1985; Singh *et al.*, 1988). Photolysed to yield free Br and BrO, bromoform may be important in the depletion of ozone from the lower Arctic troposphere at the polar sunrise (Barrie *et al.*, 1988). Ethylene dibromide and methyl bromide are significant anthropogenic sources of stratospheric bromine (ethylene dibromide is used as a grain fumigant and both are emitted in the exhaust of automobiles using leaded gasoline) but their use is declining.

Brominated trace gases in the atmosphere break down by UV photolysis and their breakdown products form BrO_x radicals which are more effective catalysts of ozone destruction than ClO_x (WMO, 1985:57; Singh *et al.*, 1988:593).

Of current but recent (Andersen, 1987) concern are the group of brominated organic compounds known by the general term halons. These are oxidised in the stratosphere and liberate bromine compounds (notably bromine monoxide, BrO) that catalyse the breakdown of ozone directly and also synergistically in concert with chlorine monoxide (ClO). For example, 20 pptv of halon 1211 (which contains one Br atom per molecule) is as (approximately) effective in depleting stratospheric ozone as 1 ppbv of Cl_x, a factor of fifty (Connell, 1986; Hoffman & Gibbs, 1988:19). Many of these trace gases, particularly the halons, have atmospheric lifetimes of decades to a century or more and even if their current levels in the atmosphere are low, may contribute significantly to the stratospheric concentrations, especially if their release continues and/or increases (WMO, 1985:64).

Halons are primarily used in fire control devices and specialized refrigeration systems. In common with some other trace constituents (e.g., CFCs), halons have the potential to affect the atmosphere in both ways: depleting stratospheric ozone and contributing to a global warming. The ozone depleting action of halons is the primary current concern but all major recent reports have addressed their possible impact on radiative transfer in the stratosphere and this concern was clearly present in the drafting of both the *Montreal Protocol* and *Canadian Environmental Protection Act (CEPA)*. Halon 1301 and halon 1211 are manufactured organohalines used

variously in fire extinguishers (small portable, fixed installations where computers and other expensive electronic equipment is used, on aircraft and also in a variety of military uses (WMO, 1985:64). Halon 2402 is included under the *Montreal Protocol* but has yet to receive comprehensive treatment in most studies because of a lack of data (see for example Hoffman & Gibbs, 1988:7).

The principal characteristics of the halons are summarized in Appendix 4. They are relatively inert, less toxic than many other chemicals used in fire control, do not obstruct visibility upon discharge, have a low electrical conductivity, corrosion, contamination and abrasion potential and are extremely effective in extinguishing fires. They therefore contribute to human survival in fires and minimise damage to expensive electrical equipment (Andersen, 1987). Indeed, it is the widespread use of electronics, particularly computer, telecommunications and electronically controlled manufacturing equipment, that has led to the extensive use of halons in fire control (Taylor, 1987). The chemical processes and reactions which enable them to extinguish fires is poorly understood but it is generally thought that bromine acts as a free radical trap, scrubbing $-OH$ and $-HO_2$ to quench the flame⁶. They are ubiquitous and at the present time are probably indispensable in a modern technological society.

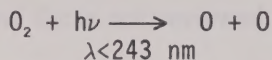
This report therefore considers the chemistry of halons as they relate to the destruction of ozone; reviews their interactions with allied species; and also attempts to summarise the future scenarios of greenhouse warming and ozone depletion in general and specifically in relation to the use and emission of halons in the context of some existing and proposed regulatory ordinances.

⁶ Evans; McFarlane, personal communications.

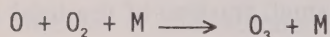
Stratospheric Ozone Chemistry

Formation of Stratospheric Ozone

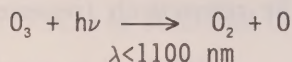
The source of stratospheric ozone is atomic oxygen produced by the photolysis of molecular oxygen by sunlight ($h\nu$)⁷. This is driven by radiation of wavelength <243 nm and takes place relatively high (>25 km) in the atmosphere.



The usual fate of the oxygen atoms is to combine subsequently with oxygen molecules to form ozone by the reaction⁸



Although ozone is rapidly photolysed by sunlight over a wide range of wavelengths according to the reaction



most of the oxygen molecules produced reform ozone by reaction with atomic oxygen (as shown above) so that the combined effect of the reaction between mono- and diatomic oxygen, and the photolysis of ozone does not result in a net destruction of ozone⁹. Because of this rapid cycling between O and O₃, their sum is a more

⁷ ν representing a solar photon.

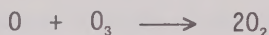
⁸ Where M is a reactant required to carry away released energy.

⁹ Text based partly upon Evans *et al.* (1987).

fundamental quantity termed "odd oxygen" (O_x).¹⁰

Catalytic Destruction of Stratospheric Ozone

The classic reaction scheme (Chapman, 1930) held that ozone is removed from the stratosphere primarily by the direct photodissociation by ultraviolet (UV) radiation and visible light (but, as explained above, the re-association of the monatomic and diatomic allotropes leads to no *net* destruction of ozone) and by the combination of ozone and atomic oxygen.

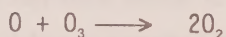


The odd oxygen is formed in the upper stratosphere by the photodissociation of molecular oxygen by shortwave (UV) radiation. These reactions between ozone and oxygen atoms account only for a small fraction of the total stratospheric ozone depletion.

Since the 1950s it has gradually become apparent that the destruction of ozone by its combination with monatomic oxygen is primarily the result of homogeneous gas-phase catalytic reactions in which the free radicals HO_x , NO_x , ClO_x and BrO_x provide the catalysts H, OH, NO, Cl and Br respectively (represented by the symbol X in the scheme below).

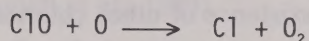
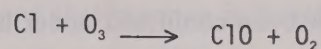


Net



which shows that while there is a net loss of ozone the catalyst is regenerated (WMO, 1985:27). Despite the importance of this reaction, specifically when chlorine acts as the catalytic halogen,

¹⁰ Below an altitude of 60 km $O_3 \approx O_x$ leading to an identification between O_3 and O_x although this is not strictly correct.



it cannot alone account for the recently reported loss of ozone from the lower stratosphere over the Antarctic and other low latitudes in the southern hemisphere because it is rate-limited by the low abundance of oxygen atoms. Several other reactions involving chlorine oxides have been proposed (Molina *et al.*, 1987; Pyle & Farman, 1987; Thrush, 1988) and these are reviewed below.

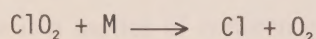
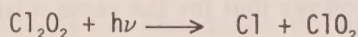
Halogen Oxide Reactions

Of particular importance are catalytic reactions involving the halogen monoxides, which further result in the regeneration of the halogen catalyst.

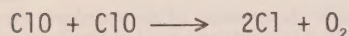
Chlorine monoxide (ClO), at concentrations two orders of magnitude greater than that predicted for 20 km altitudes at mid-latitudes, has been reported from the Antarctic (cited in Hofmann *et al.*, 1987) and undergoes both diurnal (de Zafra *et al.*, 1987) and secular (Solomon *et al.*, 1987) variation in abundance. Homogeneous (gas) phase reactions are too slow to account for the abundance of ClO which is thought to be formed as a result of reactions occurring on the ice crystals that form the Polar Stratospheric Clouds (PSCs) as described by Crutzen & Arnold (1986); McElroy *et al.* (1986) and Solomon *et al.* (1986).

The Bimolecular Chlorine Monoxide (ClO + ClO) Reaction

Molina & Molina (1987) have proposed that chlorine monoxide formed Cl_2O_2 through a termolecular reaction which is most efficient at high pressures and low temperatures and could undergo the following reactions to destroy ozone



Net



The existence of Cl_2O_2 has now been confirmed under laboratory conditions (Cox & Hayman, 1988). The possible existence of other chlorine oxides (e.g., Cl_2O_3 , ClO_0 , and the isomers $\text{ClOOC}\text{Cl}/\text{ClO}\text{ClO}$) in addition to ClO , OClO and now Cl_2O_2 have also been reviewed recently by Cox & Hayman (1988) and Thrush (1988).

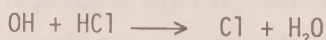
Bromine and the Catalytic Destruction of Stratospheric Ozone

Although bromine and chlorine participate as analogues in many ozone depleting reactions, there are a number of important differences in the rates at which they catalyse the breakdown of ozone. This is a function of the relative strengths of the halogen-oxygen and halogen-hydrogen bonds. The 1985 WMO report concluded that "A number of uncertainties remain in the mechanism of BrO_x -catalysed ozone destruction including the coupling with the ClO_x family through the $\text{ClO} + \text{BrO}$ reaction and the reactions controlling HBr (WMO,1985:55)". Some of this uncertainty has been since been resolved by new determinations of the important reaction rates¹¹.

The oxygen-bromine bond is weaker than its chlorine equivalent, the difference being approximately 8 kcal mole⁻¹ (WMO:1985:38), facilitating the recycling of the halogen catalyst. For example, the fast reaction of Cl with methane results in the accumulation of relatively stable hydrogen chloride



which is only slowly hydrolysed to release active Cl_x

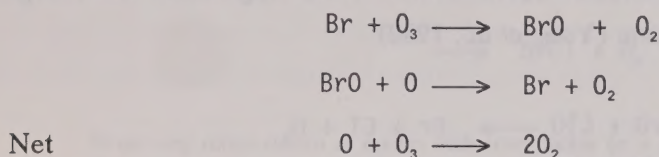


By contrast, the bromine-methane reaction is endothermic and the hydrolysis of hydrogen bromide is fast. It follows that for the same mixing ratio, more Br_x will be

¹¹ Note added in proof: see *Scientific Assessment of Stratospheric Ozone: 1989*. United Nations Environment Programme/World Meteorological Organization, 21 August 1989.

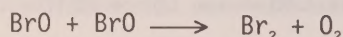
in the active form than Cl_x and that bromine is therefore a more potent¹² depleter of ozone than chlorine (McConnell *et al.*, 1989).

Bromine destroys ozone directly in the manner general to halogen catalysts (described above), specifically by the reactions:

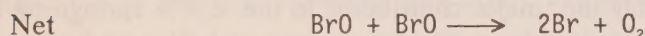
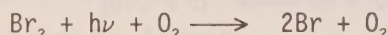


The rate of ozone destruction in the normal stratosphere caused by the $\text{BrO} + \text{O}$ reaction is limited by the low abundance of O (McConnell *et al.*, 1989) and the same constraint also applies to the other, analogous reactions of ClO and NO_2 with free oxygen.

Bromine monoxide, the principal BrO_x species in the stratosphere (according to the simulation study by Yung *et al.* (1980) not only functions in a similar manner to chlorine monoxide, but reacts even more readily as a result of the weak chlorine-oxygen bond.



The diatomic bromine undergoes rapid photolysis in the troposphere with the release of active bromine

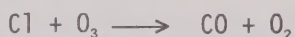


(the reaction $\text{BrO} + \text{BrO} + \text{M} \longrightarrow \text{Br}_2\text{O}_2 + \text{M}$ being relatively unimportant). It follows that despite its relatively low abundance, the increase in emissions of bromine to the stratosphere is a matter of concern given the importance of these

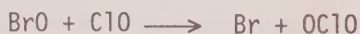
¹² An active Br is $\times 30$ -80 more efficient than one active Cl atom in destroying ozone.

reactions (WMO, 1985:38; Solomon *et al.*, 1988).

As stated above, the ClO + ClO reaction, that occurs only in the polar spring, is one of the major influences on the destruction of stratospheric ozone at those latitudes. If bromine monoxide is sufficiently abundant (McConnell *et al.*, 1989) it may react synergistically with chlorine monoxide to form oxygen and free halogens with a net breakdown of ozone (Yung *et al.*, 1980)



This speeds ozone destruction because it proceeds without the rate-limited reactions involving atomic oxygen described above and also in the absence of sunlight (see McConnell *et al.*, 1989). One branch of this reaction also leads to the formation of OCIO which accumulates during the nighttime



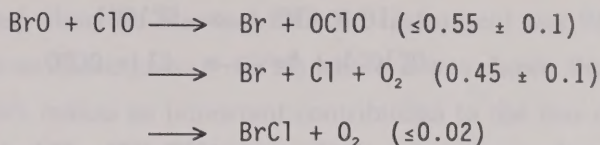
and decomposes photolytically during the day



The Cl₂O₂ reaction is probably the major contributor to the <50% springtime loss of ozone in Antarctica between 1960 and 1987 (Farman *et al.*, 1985a; Stolarski *et al.*, 1986; Hills *et al.*, 1987; Pyle & Farman, 1987; Solomon *et al.*, 1987; Salawitch *et al.*, 1988 cited by Singh *et al.*, 1988).

The BrO + ClO reaction is thought to be the main source of the observed OCIO which has been observed at twilight and polar spring and, as such, its accumulation is a major diagnostic of the abundance of active chlorine.

The products (branching ratios) of the BrO + ClO reactions as determined by Hills *et al.*, (1987) are:



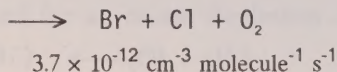
Branching ratios shown as means with error factor (σ + systematic error).
Reaction products Br + ClOO and Cl + BrOO undergo rapid thermal dissociation and are subsumed under the reaction giving Br + Cl + O₂.

The overall rate constant for product loss of the whole reaction set was

$$8.2 \pm 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

mean $\pm \sigma$ for 241-408°K, n = 114

and that for the product (calculated from the overall rate and branching ratio)

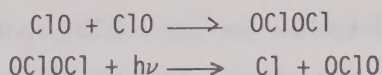


Hills *et al.* (1987) claim these reassessed constants and branching ratios will improve the inputs to simulation models and also demonstrate that the rate constants of the branch leading to Br + Cl + O₂ and the products of the BrO + ClO reaction, could account for both the rapid depletion of ozone and accumulation of OClO in the Antarctic¹³. They stress the importance of bromine in the depletion of ozone from the atmospheric column over the Antarctic.

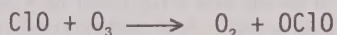
The cycle of reactions resulting from BrO + ClO leading to a net 2O₃ $\longrightarrow$ 3O₂ described on p.10 does not require either solar photons or odd oxygen to cause a depletion of ozone. Only 20 pptv Br is required to account for the abundance OClO measured in the Antarctic Spring (Tung *et al.*, 1986; Hills *et al.*, 1987; Pyle & Farman, 1987 cited Singh *et al.*, 1988) although measured values appear to be only

¹³ McConnell considers that this reaction accounts for only 10-20% of the Antarctic depletion — personal communication.

one-half to one-quarter of this (Anderson *et al.*, 1988). Molina & Molina (1987) have also proposed that the chlorine dioxide is formed by the photolysis of an isomer of Cl_2O_2 (OClOCl)

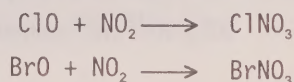


but this remains speculative (Hills *et al.*, 1987:407). Chlorine dioxide may also form slowly by the reaction

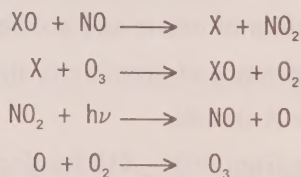


but the rate of reaction in the gas phase is not sufficient to account for the observed levels in the Antarctic although significant amounts might be produced on the surfaces of the ice crystals in PSCs (Hills *et al.*, 1987:407).

Stratospheric species of NO_x (NO , NO_2) ameliorate the ozone destroying capability of the Cl_x and Br_x as NO_2 reacts with ClO and BrO to form the relatively inert nitrates



The two halogen monoxides ClO and BrO (XO) may react with NO



which produces heating but no net loss of ozone.

It is now accepted that Cl and Br nitrates can further participate in heterogeneous phase reactions on the surface of ice or nitric acid crystals when PSCs form at -80°C , acting to release Cl_2 which then rapidly photolyze in sunlight to form two chlorine atoms that then attack ozone (Solomon *et al.*, 1988:550; Thrush, 1988).

The OC10 molecule is an important diagnostic indicator of the presence of BrO and therefore potential ozone depletion (see p.10).

The importance of BrO in ozone depletion in the mid-latitude winter stratosphere has recently been confirmed when the Harvard BrO-C10 instrument was flown on the NASA ER-2 aircraft to Great Slave Lake (~62°N) where it was shown that the C10 + BrO reaction probably makes an important contribution to the loss of ozone from the Arctic polar vortex (Brune *et al.*, 1988:561).

The reaction of the C10 molecules to form the dimer, which is of great importance in the Antarctic spring ozone depletion, is less important in the Northern Hemisphere but is of comparable significance to that of the C10 + BrO reaction. It would probably only become of concern in the high mid-latitudes at C10 abundances of ~300 pptv (Brune *et al.*, 1988:561). This is probably more than twice the abundance of C10 suggested by the OC10 levels reported by Solomon *et al.* (1988) although there are localised regions of high C10 abundance within the vortex (Brune *et al.*, 1988:561)¹⁴. At an altitude of 20 km just outside the Arctic vortex, BrO- and C10-catalysed reactions alone accounted for an ozone depletion of 0.02% daily (Brune *et al.*, 1988:561).

Halocarbons are oxidised in the stratosphere by a sequence of reactions driven by photolysis or by the reaction of the molecule with odd-oxygen O(¹D) atoms (WMO, 1985:42). The general reactions have been elucidated for chlorofluoromethanes (CFMs) which form peroxy radicals and, reacting with nitrogen dioxide (NO₂), peroxy nitrates that may act as reservoirs for NO_x in the lower stratosphere, particularly in winter and high latitudes (WMO, 1985:42). Halocarbons containing hydrogen may be slowly oxidised in the troposphere by the hydroxyl radical, the rate of the reaction ensuring that there is little breakdown in the lower atmosphere with a resulting significant transport into the stratosphere (WMO, 1985:43).

The chemistry of oxidation of halons is not well understood with respect to how well they fit this general scheme and more study is needed (WMO, 1985:43).

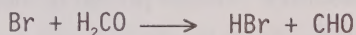
¹⁴ C10 abundances of ~800 pptv were reported in 1988 (W.F.J.Evans, personal communication).

The WMO (1985:39) report cites recent studies that indicate that the reaction between bromine and the hydroperoxyl radical

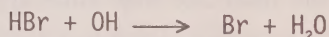


may be two orders of magnitude slower than originally thought with k_{47} values in the order $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (compare Yung *et al.*, 1980 with Posey *et al.*, 1981; Poulet *et al.*, 1984). The most recent work indicates that the reaction is much slower than first estimated by Yung *et al.* (1980) at $1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (JPL, 1987).

The reaction between bromine and formaldehyde



is one of the major sources of HBr and opposes the catalytic destruction of ozone in the lower Arctic troposphere (see following section) by depleting the atmosphere of free bromine (Barrie *et al.*, 1988). However, hydrogen bromide may act as a source of free bromine under other conditions (Barrie *et al.* (1988).



The kinetics of the bromine formaldehyde reaction



$$k_{48} \sim 1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} @ 298^\circ\text{K}$$

(Nava *et al.*, 1981; Poulet *et al.*, 1981)

and the reaction of the hydroxyl radical with hydrogen bromide



$$k_{49} 6.0\text{--}11.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} @ 298^\circ\text{K}$$

appear to be reasonably well determined (JPL, 1987) and have been used in the calculations reported in that work.

Depletion of Tropospheric Ozone in the Arctic and the Role of Bromine

The disappearance of tropospheric ozone in the Arctic, normally present at abundances of 30-40 ppb (Bottenheim *et al.*, 1986), has shown to be a recurrent phenomenon with an inverse relationship between ozone abundance and the presence of filterable bromine (Figure 1) of which 53-90% derives from gaseous hydrogen bromide, HBr (Barrie *et al.* in press cited Barrie *et al.*, 1988:138). The period of minimal ozone abundance and maximum ozone variability also correlates with the March-April polar sunrise (Oltmans & Komhyr, 1988) and the fall in concentration of the most common alkanobromine, bromoform CHBr_3 .

Barrie *et al.* (1988) postulated that bromoform is released by decaying red benthic marine algae in the Arctic. Wever (1988) has since pointed out that temperate latitude brown algae release a number of volatile organic compounds including bromoform ($\sim 10^4 \text{ t y}^{-1}$). This release is an active metabolic process under the control of an enzyme system having a vanadium prosthetic group. The two species studied (*Ascophyllum nodosum*, *Fucus vesiculosus*) showed marked seasonal variability with maximum production in the winter and spring and a rapid decrease in summer. If Arctic species possess similar metabolic pathways, they might provide a source of bromoform sufficient to account for the observed decrease in tropospheric ozone.

Barrie *et al.* (1988) propose that in the Arctic winter, the ozone of the boundary layer over the ice cap is isolated from the ozone of the upper troposphere by a strong radiation inversion which also traps a variety of natural organobromines. At the polar sunrise, these compounds (notably bromoform) are photolysed liberating ozone depleting BrO_x species and causes a total loss of ozone which cannot be replenished from above the inversion. Their scheme eliminates dry deposition as a cause of ozone depletion in favour of a chemical and dynamical explanation.

Their tentative chemical scheme is discussed *inter alia* above in the sections on chemistry. Although they consider naturally generated bromoform is the major

source of HBr they argue that other precursors also exist. There are few data on organobromines in the Arctic (see Khalil *et al.* 1986) but, given the extensive pollution of the Arctic air mass, especially in the last three or four decades, there must be concern over the emission of any additional bromine into the region.

Halons¹⁵

Halons are fire suppressants and extinguishants that are in widespread use because of their effectiveness; low electrical conductivity (which leaves electronic equipment and plant undamaged); lack of harmful residue (which also reduces the need for clean-up following use) and, in the case of halons 1211 and 1301, relatively low human toxicity (HRI, 1988a). The concern over their emission to the atmosphere results from their chemical nature as fully saturated, halogenated organic compounds which contain at least one bromine atom in the molecule. This confers the properties of persistence in the atmosphere sufficient to ensure their transport to the stratosphere where they contribute to the processes of ozone depletion and greenhouse warming.

The potential for a compound to destroy stratospheric ozone is expressed by its Ozone Depletion Potential (ODP)¹⁶ index (the ratio of the substance's ability to destroy ozone compared with that of CFC-11). Their high values indicate that each halon molecule reaching the stratosphere is much more potent in destroying ozone than CFCs. The need is to determine whether the atmospheric abundance of halons is likely to increase sufficiently to realise this potential.

Quantification of the production, use, banking and emission of halons are essential to any assessment of their environmental impacts but such information is difficult to obtain. This is partly because halons are proprietary compounds and their production and sales have, until recently, not been widely published by the industry, especially because their environmental impact has only lately become of concern. Some of the halons, particularly halon 2402, are of strategic importance and details of the amounts used and the manner of their deployment has not been public knowledge. There are several manufacturers, often with plants based in both

¹⁵ The physical and chemical properties, and other information on halons are summarised in *Appendix II*.

¹⁶ The ODP incorporates the molecular weight and atmospheric lifetime of the compound relative to those of CFC-11, together with the number of Cl atoms and other halogen (e.g., Br) in the molecule. Other halogens are qualified by a function (α) which expresses the ozone-depleting potential of that element relative to that of the Cl atom. Values of α range 35-80 for Br.

N. America, Europe and Japan. In some instances there may be a complex pattern of import and re-export of halon between sectors. Consequently it is difficult to obtain reliable data on global production, banks, emissions etc. and many of the published values are inevitably approximations and dependent upon many assumptions. This situation is complicated further by the dearth of information on halons in the Soviet Union and other eastern bloc nations. As part of its response to the growing awareness of the environmental effects of halons the industry is coordinating data on halon use and emissions (HRI, 1988a). The weakness in the data base of halon production, emissions and banks is evident from the compilations included as tables and figures in this report and the values adopted by various authors in making assessments of halon impacts on the atmosphere.

There are problems in relating production, emissions and atmospheric abundances because of the existence of large halon banks. Large quantities of halon are stored, or banked — the majority of halons that have ever been produced are currently banked — in fire control equipment. For some halons, the bank lifetime may be forty years, introducing a large temporal buffering factor into any attempt to quantitatively relate production, use, emissions and atmospheric abundance. Future scenarios, which are dependent on the reliability of the source functions used in computer simulations, are particularly sensitive to assumptions concerning the fate of the halon buffer, for example what portion of the bank will be released to the atmosphere and what portion will be re-used or recycled and the timing and rates of such processes. Finally, it is important to note that the atmospheric abundances for halons are very close to detection limits of the currently available instrumentation. It should also be noted that with the exceptions of the simulations by Hoffman & Gibbs (1988) and McConnell *et al.* (1989), the published studies on future scenarios do not reflect the situation post-1987 and the ordinances of, for example the *MP* and the regulations of the EPA and *CEPA*.

Halon 1211

Characteristics

Halon 1211 has a high boiling point and low vapour pressure making it suitable for local application in portable fire extinguishers because it can be discharged in a directional manner (Andersen, 1987). Bromine is an extremely effective inhibitor of combustion and halon 1211 can cause rapid extinction of fires (WMO, 1985:73).

It is not suitable for total flooding situations because of its toxicity, harmful effects being manifest at concentrations approximately one-third those required to extinguish fires¹⁷, the critical dose being 2% by volume exposure <1 min (Taylor, 1987). It is considered a "clean" extinguishant and is used for costly electronic equipment, in aircraft, printing presses and museum and archive applications (Taylor, 1987).

Development, Production and Use

Halon 1211 was developed in the middle 1960s as a replacement for carbon tetrachloride and carbon dioxide in portable fire extinguishers and has supplanted them since the early 1970s (WMO, 1985:73).

ICI Ltd. (a major manufacturer) reports that the initial high production rates have not been maintained but also admits that there appear to be no reliable data (cited, WMO (1985:73). A more recent assessment by this company shows that European and N. American annual production in the period 1978 through to 1987 increased from 6,487 t to 13,588 t with considerable year-to-year variability (Table 1). The 1985 U.S. production plus imports was 2,818 t leaving 2,750 t after exports (Anderson, 1987 and Table 2). Andersen (1987), reviewing U.S. EPA assessments based on industrial estimates, shows that the demand almost doubled between 1981 (1,118 t) and 1984 (2,196 t) and, *in the absence of controls*, might exceed 12,000 t by the year 2,000 (Table 3). Extrapolation from atmospheric concentrations suggest that (global) production is approximately 5,000 t y⁻¹ (see below and WMO, 1985:64,73). Hammitt *et al.* (1987) used a value of 3,000 t y⁻¹ in their simulation (see Table 4).

¹⁷ Taylor, personal communication.

The 1986 U.S. load (load = domestic production + imports - exports) was 2,750 t according to industry sources (Table 2).

Banks and Emission to the Atmosphere

The 1985 emissions were estimated to be 15% of the total sales (EPA estimates reported by Andersen, 1987; see also Table 2).

The service lifetime is approximately 30 y (Hoffman & Gibbs, 1988:54) to <40 y (Singh *et al.*, 1988).

Large quantities are banked in fire extinguishing systems but the storage/bank time is probably less than that of halon 1301 (Anderson, 1987; Hoffman & Gibbs, 1988:19; Tables 3 & 5). The industrial scenarios reviewed by Andersen (1987) suggests that the halon 1211 bank grew from 1,342 t in 1978 to 16,345 t in 1988 and could, *presumably in the absence of controls*, exceed 76,000 t by the year 2,000 (Table 22).

Relatively little (26.5% total emissions) halon 1211 is released in fire control, most being released to the atmosphere during production; accidental leakage; inadvertent discharge at disposal and in decommission programmes (Andersen, 1987; Singh *et al.*, 1988:594). The largest cause of emission (52% of the total) results from releases during training programmes, a quantity that is in excess of 8% of the annual U.S. load (Table 2).

Stratospheric measurements were made first in 1982 and also in the two following years by Lal *et al.* (1985). From this the WMO concluded that there had been a rapid increase in halon 1211 emissions of 20 per cent *per annum* in the lower stratosphere (WMO, 1985:637). Recent studies by Singh *et al.* (1988) consider the increase to be closer to 12% annually (see Table 6 and following text).

Extrapolating back from data on the annually increasing atmospheric abundances of ~12-20% suggest that global releases to the atmosphere would be 2,200-3,600 t annually (Lal *et al.*, 1985; Singh *et al.*, 1988 & Table 7). The EPA emission scenarios reviewed by Andersen (1987) are higher but are within this general range although future predictions are probably unrealistic in light of proposed controls (Table 3). McConnell *et al.* (1989) noted the 3,000 t y⁻¹ suggested by Hammitt *et al.* (1988) and

other published values and adopted a basic scenario for their modelling study in which there was a linear increase from zero in 1966 to 4,000 t y⁻¹ in 1976 after which emissions stabilised at that level. To allow for the provisions of the *MP*, which freezes halons at the 1986 production figures, they also ran simulations in which emissions reached 1986 production levels by 2006 (other factors such as CFCs, methane and nitrous oxide remaining unchanged between the two scenarios). These simulation studies are discussed in greater detail under the sections dealing with *Future Scenarios* and *Contribution of Halons to Ozone Depletion* that follow.

About 10% halon 1211 used on fires is converted to non ozone-depleting compounds in the fire (Andersen, 1987).

Atmospheric Abundance

Tropospheric profiles taken in 1979 at 70°N are shown in Figure 2 (the figure taken from the WMO, 1985:639 report is a composite of data by Rasmussen & Khalil, 1983b and Lal *et al.*, 1985). Concentrations have been reported at 1.1 ± 0.1 pptv at 72°N in 1983 (Rasmussen & Khalil, 1984c; WMO, 1985:636; Table 8) and in 1984 as 1.5 pptv (tropopause) and 0.03 pptv (23 km) by Lal *et al.* (1985). Measurements by Lal *et al.*, (1985) found that the abundance decreased by two orders between 15 km and 25 km in altitude.

Concentrations of halon 1211 in the atmosphere have been increasing at 10-30 per cent yearly at the Antarctic, Arctic and Oregon (Khalil & Rasmussen, 1985c) and also in the upper stratosphere over France (Lal *et al.*, 1985). The WMO report also cites a communication from Lovelock in 1985 that ambient levels of halon 1211 over Cornwall, U.K. increased from 0.16 pptv in 1978 to 0.43 pptv in 1980 and 1.5 pptv in 1981. In 1987, Singh *et al.* (1988) established profiles through the troposphere and stratosphere at latitudes 44°N and 17.5°N (Figure 3 & Table 9) and compared the abundances (tropospheric volume mixing ratio 1.96 pptv) with those established by Lal *et al.* (1985) leading them to suggest that halon 1211 was probably increasing at approximately 12% yearly, rather than the 20% suggested by Lal *et al.* (1985). They stress that these projections must remain approximate whilst there is a paucity of data and atmospheric concentrations approach the detection

limit of the currently available instrumentation. Data from the South Pole (Khalil & Rasmussen, 1985c) suggest that halon 1211 increased over a six year period at $\sim 22 \pm 5\%$ annually (WMO, 1985:75).

The 1984 level in the Arctic was about 30 per cent higher than that in the Antarctic (1.1 pptv) reflecting the predominant use of halon 1211 in the industrialised countries of the Northern Hemisphere (WMO, 1985:75).

Like most other trace halocarbons (see Fabian *et al.*, 1985), the vertical profile of halon 1211 in the mid-latitude profile shows a step or inflection, the abundance falling off to $\sim 50\%$ with increasing altitude. At low latitude there is a more gradual decrease in abundance with height attributed to the greater stratospheric mixing resulting from tropical upwelling.

If use and emission increases at the 1985 rate for a decade, the concentration of halon 1211 would exceed 10 pptv and contribute more bromine to the stratosphere than known natural sources (WMO, 1985:75).

Atmospheric Sinks

Halon 1211 is removed from the atmosphere only by UV photolysis (Singh *et al.*, 1988:594). Because it has a higher absorption cross section (10^{-22} cm^2) beyond a wavelength of 290 nm than halon 1301, it also undergoes photolysis in the lower troposphere (Molina *et al.*, 1982 cited Singh *et al.*, 1988:594). This leads to a shorter atmospheric lifetime, slower build up and faster recovery following a cessation of emission than would occur for halon 1301.

Atmospheric Lifetime

An atmospheric lifetime of 29-42 y was suggested by Lal *et al.* (1985). Many authors have used a value close to 25 y (Molina *et al.*, 1982; Prather *et al.*, 1984; NAS, 1984 cited by the WMO, 1985:70,75; McConnell *et al.*, 1989 and Table 7).

Connell (1986) estimated the *e*-folding lifetime¹⁸ at 12.9 y (Table 10). From this it follows that it would take 39 y and 60 y for halon 1211 to fall respectively to 5%

¹⁸ The "e-folding lifetime" is the period after which the abundance has declined by $1/e$, or to approximately 37% of its original value.

and 1% once all emissions ceased.

Hammitt *et al.* (1987:711) used a value of 12.5 y in their simulation, defining atmospheric lifetime as the steady state atmospheric burden/constant emission rate (Table 4).

Ozone Depletion Potential

An Ozone Depletion Potential or Efficiency (ODP, ODE)¹⁹ of 2.7 has been adopted by Hammitt *et al.* (1987) and Singh *et al.*, (1988:594) although some authors have used a value of ~2.4.

Connell (1986) proposed that *on a molar basis* halon 1211 is about twice as effective as halon 1301 in depleting stratospheric ozone (20 pptv halon 1211 $\approx$ 40 pptv halon 1301, see Hoffman & Gibbs, 1988: 1988) although the ultimate impact of the latter is much greater because of its long stratospheric residence time. Halon 1211 probably contributes 2% to the overall ozone depletion resulting from anthropogenic chemical emissions to the atmosphere (Andersen, 1987).

Future Scenarios

Hoffman & Gibbs (1988) undertook a 1-dimensional simulation (based on the model of Connell, 1986) and using a variety of emissions projections based on those of the EPA (1988) to examine a series of plausible scenarios. These included: no controls; *Montreal Protocol*; Total global freeze and additional projections covering different mixes of CFCs and their substitutes together with varying extents of national/regional participation. Their results indicate that, in the absence of controls, halon 1211 would increase from ~1 pptv in 1988 to approximately 28 pptv and 32 pptv by the years 2075 and 2100 respectively (Hoffman & Gibbs, 1988:19, Table 11, Figure 4). Because of its relatively short service and atmospheric lifetimes, atmospheric levels would stabilise at 6 pptv by 2075-2100 under the provisions of the *Montreal Protocol* (Table 11, Figure 4).

¹⁹ The O_3 depletion per unit mass chemical/ O_3 depletion per unit mass CFC-11.

Hammitt *et al.* (1987) undertook an extensive review and simulation of future scenarios for a range of Potential Ozone Depleters (PODs) including halon 1301 and 1211. This was based upon a review of individual chemical scenarios, including historical factors governing use in three major geographical sectors; scenarios for economic growth and POD usage integrated with respect to geography and POD application to provide a statistical probability for Gross Global Production (GGP) and POD; production scenarios encompassing growth rates weighted for according to individual growth rates, ODP taking into account shifts in usage pattern over time and emission scenarios taking into account the loose coupling between production and emissions.

The results of this analysis are qualified by a "score function" assigning a probability to any given value and used as an input to the 1-D Lawrence Livermore National Laboratory (LLNL) atmospheric simulation model often used in ozone depletion studies.

Ozone depletion resulting from all trace gases is the primary focus of the study, rather than the specific scenarios and impact of halons. The results are summarised in Table 12 and show estimated production, emission and surface abundances for halon 1211 for the years 1985, 2000 and 2040 and with CFC-11 and CFC-12 capped at 1985 levels. Each datum is ascribed a probability ("quartile of the score function") indicating the reliability of the estimate.

Depending upon the assigned probability, surface abundances were in the range 3.32-4.50 pptv for the year 2000 and 14.9-46.9 pptv by 2040 (Hammitt *et al.*, 1988) did not simulate the provisions of the *Montreal Protocol*.

The simulation of Hoffman & Gibbs (1988:23,54, Figure 5) suggest that only a complete ban with complete global compliance would reduce the atmospheric abundance of halon 1211 to below 1985 levels and then not until about 2040. It is important to note that the study by Hoffman & Gibbs (1988) do not make allowance for the possible recovery and destruction of halon banks, measures that if implemented, could substantially reduce the atmospheric abundance below the simulated levels.

The simulation study by McConnell *et al.* (1989) examined a number of scenarios for halon emissions (variously in concert with other ozone-depleting substances e.g., CFCs, methane, methyl chloroform and nitrous oxide). This included a *MP* case study in which halon emissions were fixed at a nominal 1986 value of $3,000 \text{ t y}^{-1}$ and a "modified" case in which it was supposed that although production was stabilised at $\sim 10,000 \text{ t y}^{-1}$ under the *MP*, continuing emissions from the bank would eventually rise to meet this production value (i.e. production = emission = $10,000 \text{ t y}^{-1}$). This is only one of a number of plausible scenarios but is significant because it is the first attempt to address the fate of the industrial halon bank on atmospheric halon abundance and ozone depletion.

The simulated abundances of halon 1211 were slightly lower than current measured values, the difference being considered unimportant (Figure 6). The tropospheric abundance increased steadily to stabilise at a mixing ratio of 3.2 pptv under their *standard MP* scenario and at 7.8 pptv under the modified scenario (Figure 7). Above 10 km altitude the abundance diminished, falling an order of magnitude between 15 km and 25 km (Figure 8). This is again lower than the measured values (which show a drop of two orders of magnitude between these altitudes, e.g., Lal *et al.* 1985). The discrepancy was attributed to the limitations of the 1-D model in simulating various transport processes above an altitude of 20 km and to the value of K_z selected.

The effect on the integrity of the stratospheric ozone layer is considered in the section *Contribution of Halons to Ozone Depletion* that follows.

Halon 1301

Characteristics

Because halon 1301 mixes well with air and has a low boiling point and high vapour pressure it can be discharged rapidly making it suitable for use in circumstances when enclosed spaces must be completely flooded by extinguishant (Taylor, 1987). Compared with halon 1211, it has a relatively low human toxicity, the toxic level

being approximately the same as that required to extinguish fires²⁰. Exposure is tolerated at a level of 5% halon 1301 (sufficient to extinguishes most fires) <10 min (Taylor, 1987). It is primarily used in fixed installations where water and carbon dioxide are inappropriate (e.g., computer rooms, magnetic tape libraries, marine engines, naval applications, particularly on aircraft carriers, art storage). Some is also used as a specialised refrigerant. In recent years its use has increased in fire protection of large oil and gas pipeline pumping facilities (WMO, 1985:73; Taylor, 1987).

Development, Production and Use

The industrial production of halon 1301 is thought to be increasing (WMO, 1985:43) but all assessments are hindered by the fact that "No information on world wide release rates of halons ... or on global production figures is available" (Singh *et al.*, 1988:595).

The 1976 global production was estimated to be 1,400-3,000 t (WMO, 1985:73) increasing to an estimated 7,000-8,000 t by 1984 (1978 and 1985 estimates by DuPont reported by the WMO, 1985:73). The joint European and N. American production increased from 2,823 t in 1978 to 7,690 t in 1987, the year-to-year increases varying considerably (Table 1). The 1976 U.S. production was estimated to be 1,400 t increasing to 3,600 t by 1985 (Andersen, 1987).

The increase reflects the use of halon 1301 in the petrochemical industry (see above). DuPont anticipates a decrease in the extent to which halon 1301 is used for fire protection in the future (WMO, 1985:73). Andersen (1987), reviewing EPA scenarios, suggests that demand could double in the 5 years from 1985 to 1990 although such predictions do not appear to reflect the provisions of the *Montreal Protocol* or other control measures (Table 5). Approximately 7% of the 1986 U.S. load was used in fire control (Table 2).

²⁰ Taylor, personal communication.

Banks and Emission to the Atmosphere

The service lifetime is approximately <40 y and large quantities are banked in fire extinguishing systems. This extensive bank (e.g., ~25,000 t) will probably result in protracted releases into the atmosphere for many years (Hoffman & Gibbs, 1988:19).

Emissions accounted for 30% of total sales in 1985 (Andersen, 1987). In addition to its release in fire control, the compound is emitted to the atmosphere as a result of product development, leakage, inadvertent discharge at disposal and decommissioning and in training programmes (Singh *et al.*, 1988:494). The greatest cause of emissions (51% total emissions) was unwanted discharges and discharge tests of fire control installations (Table 2).

Extrapolating back from data on atmospheric abundance which are increasing at ~4.5% y⁻¹, Singh *et al.* (1988:595) suggest that global releases to the atmosphere would be 1,210 t annually. This is in general accord with the EPA estimates reviewed by Andersen (1987) of 1197 t in 1976 (Table 5). The simulation by McConnell *et al.* (1989) pegged emissions at half the halon 1211 level but otherwise adopted a similar scenario in which emissions increased linearly from zero in 1966 to a maximum of 2,000 t annually by 1976 after which it stabilised at that value.

About 1% of halon 1301 used in fires is converted to non ozone-depleting substances (Andersen, 1987).

Atmospheric Abundance

The first tropospheric concentrations (0.7 pptv) were made by Penkett *et al.* (1981) and the first stratospheric profile determined in 1980 by Fabian *et al.* (1981a), these are shown in Figure 2.

The 1987 programme of Singh *et al.* (1988) established profiles through the troposphere and stratosphere at latitudes 44°N and 17.5°N (Figure 9, Table 13) and compared the abundances (tropospheric volume mixing ratio 1.3 pptv) with those established by Fabian *et al.* (1981) and Penkett *et al.* (1981) leading them to suggest that halon 1301 was probably increasing at approximately 4% yearly (Table 6). Again, such projections must remain approximate whilst there is a paucity of data and atmospheric concentrations approach the detection limit of the currently

available instrumentation. This is less than the increase in halon 1211 but, given the long lifetime and efficiency in ozone depletion (four times greater than that of halon 1211), it remains a cause of considerable concern.

At low altitudes, there was little difference in concentration between the low and mid-latitudes whilst at high altitudes the abundance was greater in the tropics than at mid-latitude.

The numerical simulation by McConnell *et al.* (1989) reproduced current and recent tropospheric abundances (Figure 6) well and shows that the abundance declines by a "factor of three" between the altitudes of 15 and 25 km (Figure 10).

These simulation studies are discussed in greater detail under the sections dealing with *Future Scenarios* and *Contribution of Halons to Ozone Depletion* that follow.

Atmospheric Sinks

Because it has a negligible absorption cross section ($\ll 10^{-22} \text{ cm}^{-2}$) beyond a wavelength of 290 nm halon 1301 does not photolyze in the troposphere but is slowly removed in the stratosphere under the impact of the 190-285 nm UV radiation (Molina *et al.*, 1982 cited Singh *et al.*, 1988:594).

Atmospheric Lifetime

Halon 1301 has a long residence time in the atmosphere of 80-110 y (Molina *et al.*, 1982; Prather *et al.*, 1984; WMO, 1985:70,75; McConnell *et al.*, 1989 and Table 7) suggesting that the maximum that will be reached is greatly in excess of the current measured abundances.

Connell (1986) estimated the *e*-folding lifetime at 100.9 y (Table 10). From this it follows that it would take 303 y and 465 y for halon 1211 to fall respectively to 5% and 1% once all emissions ceased.

Hammit *et al.* (1987:711) used the value of 100.9 y in their simulation, defining atmospheric lifetime as the steady state atmospheric burden/constant emission rate (Table 4).

Ozone Depletion Potential

An ODP of 11.4 has been adopted by Hammitt *et al.* (1987) and 11.7 by Singh *et al.* (1988:594).

At equivalent molar concentrations, halon 1301 is slightly less effective in depleting stratospheric ozone than halon 1211 (see Hoffman & Gibbs, 1988:19) but the ultimate impact of halon 1301 is much greater because of its long stratospheric residence time which leads to much greater atmospheric abundances.

For example, although the 1985 U.S. production was 3,600 t, this is equivalent to 41,000 t when weighted for its high ODP in comparison to CFC-11. Halon 1301 accounts for 12% to the total ozone depletion caused by anthropogenic chemical emissions when this weighting is applied (Andersen, 1987).

The effect on the integrity of the stratospheric ozone layer is considered in the section *Contribution of Halons to Ozone Depletion* that follows.

Future Scenarios

Ramanathan *et al.* (1985) propose that the 1980 level of halon 1301 will increase from 1 pptv to a probable value of 5 pptv (with a possible range of 3-10 pptv) by the year 2030. The results of the study by Hammitt *et al.* (1987) are summarised in Table 12 and show estimated production, emission and surface abundances for halon 1301 for the years 1985, 2000 and 2040 and with CFC-11 and CFC-12 capped at 1985 levels. Depending upon the assigned probability, surface abundances were in the range 4.99-6.73 pptv for the year 2000 and 22.8-80.6 pptv by 2040. The study did not simulate the provisions of the *Montreal Protocol*.

The simulation (see p.22) by Hoffman & Gibbs (1988) indicate that under the provisions of the *Montreal Protocol*, halon 1301 will increase from ~1 pptv in 1988 to 13 pptv and 16 pptv respectively by the years 2075 and 2100 but would reach respectively ~40 pptv and ~68 pptv in the absence of controls (Table 11, Figure 4).

The implementation of the *Montreal Protocol*, with halon 1301 production fixed at 1986 levels, will not result in a stabilization of its atmospheric concentration (Hoffman & Gibbs, 1988:19, Figure 4).

With a 90% reduction and 100% participation in the *Montreal Protocol*, levels could stabilise by about 2030 but a 100% reduction and 100% participation implemented by 1990 would be required to substantially reduce atmospheric abundances and this would not cause a fall in atmospheric abundance below 1985 levels in the foreseeable future (Hoffman & Gibbs, 1988:23,53, Figure 11).

The simulation by McConnell *et al.* (1989) found that for the 2,000 t annual emission scenario, under the provisions of the *MP*, that tropospheric abundances stabilised at 4.5 pptv. For the modified scenario where production = emission = 10,000 t y⁻¹, tropospheric abundances of halon 1301 increased greatly to stabilise at 22.5 pptv (Figure 7). Although emissions were fixed at half of those for halon 1211, the long (~ x3) atmospheric lifetime of halon 1301 resulted in its ultimate abundance exceeding that of halon 1211 for both the standard and modified cases. The abundance declines by a "factor of three" between the altitudes of 15 and 25 km (Figure 10).

Again, recovery and destruction of halon banks could reduce the atmospheric abundance of halons below the levels indicated by these simulations.

Halon 2402

Characteristics and Use

There is relatively little accessible information about halon 2402 (Buxton, 1978).

The human toxicity is approximately one-tenth the atmospheric concentration required to extinguish fires (13% v/v lethal; maximum acceptable exposure 0.05% v/v, 500 ppm for 10 min or 0.1% v/v, 1,000 ppm for 1 min). The principal toxic effect is to sensitize the myocardium to catecholamines (adrenaline, epinephrine; noradrenaline, norepinephrine) and in this regard it is one of the most potent of such substances²¹.

The toxicity requires that it be used only in situations that are not normally occupied or in outdoor locations. It is rarely used for fire control in the U.S.A. and

²¹ McFarlane, personal communication; Correspondence from R.P.Gallucci (DuPont) to J.Ziemba (NAFED).

is proscribed for such purpose in some European countries¹⁴. The Japanese and Soviets use some halon 2402 in small, portable fire extinguishers and it is used extensively for the fire protection of shipboard machinery, petrochemical plant in the Soviet Union. It is used as a roof seal in oil storage tanks in the U.K. and as a fabric fire retardant in Italy and for cleaning agent in semiconductor production in Japan.

Halon 2402 is classed as a strategic chemical in the U.S.A. and is used by both superpowers to control the burn in rocket engines²², stabilising the flight of ballistic missiles¹⁶.

Development and Production

Daikin Kogyo Co. Ltd. of Japan (who hold the patent) and Montecatini-Edison in Italy monopolize halon 2402 production although it is not clear whether the Soviet Union has a manufacturing facility. The Soviets used to purchase halon 2402 from Japan and Italy but since the proscription of sales from the West it was assumed that they had undertaken manufacture themselves¹⁵. Recent evidence, that officials of the Japanese Daikin corporation had been selling halon 2402 illegally to the Soviet Union²³, suggests that this might not be so. It is not clear if the Soviet Union was obtaining all its halon 2402 from Japan or whether it has some manufacturing capability of its own and was importing only the extremely pure (>99.8%) distillate from Daikin.

Service Life and Emission to the Atmosphere

The increase in atmospheric concentration of halon 2402 over recent years (see below) presumably reflects its use and manufacture in the Soviet Union, activities for which no direct data are available²⁴.

²² Taylor, personal communication.

²³ PREDICAST Newsletter Database, © Kyodo News International; Japan Computer News Industry Scan.

²⁴ Taylor, personal communication.

Atmospheric Abundance

There are few data on atmospheric abundances of halon 2402 but concentrations are reported to have increased by 25-26% in recent years, almost certainly because of emissions from Soviet sources²⁵.

Ozone Depletion Potential

The ODP is approximately 6²⁶.

²⁵ McFarlane and Taylor, personal communications.

²⁶ Taylor, personal communication.

Contribution of Halons to Ozone Depletion

Exactly how much halons will contribute to the global stratospheric ozone depletion is not clear because the size of that depletion is inevitably more a function of the availability of Cl_x derived from CFC emissions and both the production and emission of CFCs and halons will alter in the near future. Further, few of the simulations undertaken to date have examined the effect of the CFC and halon controls required under the *MP* and those that have did not examine the important problem of how the halon bank is to be managed.

The extensive simulation by Hoffman & Gibbs (1988) concluded that even under the provisions of the *MP* atmospheric abundances of halon 1211 and 1301 will grow to 6 pptv and 13 pptv respectively by 2,075 and that only a complete ban on halon 1301 and 90-100% ban on halon 1211 would enable their levels to stabilise.

Similarly, McConnell *et al.* (1989) showed that against the background effects caused by other substances (e.g., CFCs whose emissions are controlled as required by the *MP*), halons contribute only slightly to the column ozone depletion ozone in the short term but that the effect of halons increases with time to contribute 1.2% to the steady state depletion of 5.2% (compare curves A & B, Figure 12). Their modified scenarios, in which emissions were set at $10,000 \text{ t y}^{-1}$ (see above) led to much more severe depletions <9.2% at steady state (compare curves BB and CC, Figure 12). The moderating effect of methane and nitrous oxide on total column ozone (scenarios C and CC, Figure 12) reflect an increase in tropospheric ozone following the oxidation of methane and partially masks a severe depletion of ozone in the stratosphere. The impact of halons is manifest primarily at altitudes of 15-25 kilometres (Figure 13).

McConnell *et al.* (1988) concluded that, even under the provisions of the *MP*, there could be a steady state column depletion of ~6% of which half could be caused by halons.

Clearly bromine released in the stratosphere by the breakdown of halons presents a threat to the integrity of the ozone layer. Their effect appears to be significant, how significant will depend upon a broad based research agenda on the role of

bromine in the atmosphere and particularly on the numerical simulation of a wide range of scenarios that particularly address the fate of the large and growing amount of halon banked in fire suppressing systems.

Halons, Bromine and the Greenhouse Effect

The spectral range and band intensity of halon 1301 has been estimated by Pugh & Narahari Rao (1976) and is cited by in WMO (1985:831) and Table 14. Its absorption in the 7-13 μm window suggests that it might contribute to a substantial surface warming if its atmospheric concentration increases sufficiently (WMO, 1985:854). Calculations by Ramanathan *et al.* (1985) suggest that for each ~ 1 ppbv increase in concentration through the column 0-12 km the surface temperature would increase by almost 0.2°K (see also WMO, 1985:857 and Figure 14). The simulation by Hoffman & Gibbs (1988:12,35) confirm the potency of this compound in radiative forcing (Figure 15). From this it is clear that for a given increase in concentration, halon 1301 may exert a more powerful warming effect than many or most of the CFCs and a number of other trace gases — especially as the effects of individual gases are additive and halon 1301 has an atmospheric lifetime of 100-110 y (WMO, 1985:22). However, in terms of the maximum mixing ratios expected from the *MP* scenarios discussed above (i.e., ~ 22 pptv), the surface temperature increased would only be about 0.004°K . By convention, a radiatively active gas may be considered a serious agent of climatic warming only if its atmospheric abundance reaches levels that induce a change in the order of $\Delta + 0.1^\circ\text{C}$.

Although there would not appear to be grounds for great concern over the climatic forcing effects of halons, some *caveats* should be borne in mind. For example, there is considerable uncertainty over the future pattern of halon production and emission to the atmosphere, particularly with respect to the fate of the halon banks. It is possible therefore that halon emissions might be much greater than expected. In assessing the warming potential of halons it should also be recognised that there are a large number of so-called greenhouse gases, many of which do not cause a great impact on their own, but which might have to be individually controlled as part of the amelioration of their overall effects. Finally, compliance with 35e *Montreal Protocol* allows trade-offs to be made between various ozone depleting compounds based upon their ODPs (relative Ozone Depleting Potential). Although the authors of the Protocol were "conscious of the potential

climate effects of...emissions" it is possible that such trade-offs as may be desirable with respect to ozone depletion could lead to a less optimal mix of RAGs and exacerbate the radiative forcing problem (Hoffman & Gibbs, 1988:12).

Control of Atmospheric Bromine Liberated from Halons

Most of the national and international initiatives concerned with environmental impacts of CFCs and halons has been directed toward controlling production, ideally leading to a phase-out and complete proscription. With respect to halons, for which there are no obvious alternatives and for which substitutes may not be available for a decade, there seems to be considerable scope for limiting unwanted emissions (i.e., halons released to the atmosphere for reasons not directly connected with fighting fires). The fate of the large amount of halon stored or banked in fire control systems is also of great importance and the management of that bank bears scrutiny.

Sources of Emissions: Operational Considerations

Halon manufacturers and users are evaluating systems and operations with respect to controlling emissions to the atmosphere (Willey, 1987). From their perspective, the emergence of the halon/ozone-depletion issue has been "sudden and unanticipated" and the industry — notably the Halon Research Institute (HRI), National Fire Protection Association (NFPA), Fire Equipment Manufacturers Association (FEMA), National Association of Fire Equipment Distributors (NAFED) and Fire Suppression Systems Association (FSSA) — rapidly organized to collect data on halon use through Halon Fire Extinguishing Agent Statistical Committee (Andersen, 1987).

The NFPA's Committee on Halogenated Fire Extinguishing Systems had proposed mandatory full-discharge testing of halon 1301 installations under its ordinance *NFPA 12A*, Halon 1301 Fire Extinguishing Systems. This practice had been common, but not universal, contributing greatly to the largest single cause of halon 1301 emissions (full discharge tests account for 31% of total emissions compared with the 23% resulting from use on fires (Table 2). The full-discharge test was recommended because the required concentration of halon 1301 is often not maintained for the specified period following discharge (the concentration holding time), a fact unacceptable to insurers who demanded more thorough operational checks (Taylor, 1987). Following representations from the Environmental Protection Agency (EPA) and other bodies during the period of public comment on the new

test protocol, manufacturers and the industrial organizations voted overwhelmingly against the proposal, leading the NFPA to abandon the mandatory requirement (Andersen, 1987; Taylor, 1987). The industry then placed the search for alternative testing procedures as priority and has subsequently revised *NFPA 12A*. In addition, the NFPA is publicising the environmental concerns that attend the use of halons and the National Fire Protection Research Foundation (NFPRF) are developing methods for reducing emissions from testing, training and accidental release. There is also a joint working committee of the U.S. Department of Defense (DoD) and the EPA to consider releases from military installations, the military being a major user of halons (Andersen, 1987).

Given the large proportion of halons emitted in testing programmes there has been considerable interest in the development of surrogates that behave in similar fashion to halons, permitting adequate and realistic operational testing of fire control installations with reduced environmental impact. At present, halon 121/HCFC-22 and sulphur hexafluoride (SF_6) are being tested by the NAFED and the HRI as possible replacements for halon 1301 in systems testing (EDF, 1988; HRI, 1988b)²⁷.

It is recognised that the concentration holding time (the maintenance of the required halon concentration for the required period following test of a fixed fire control system) is governed more by the integrity of the enclosed space than the delivery system's efficiency. Most of the delivery systems are extremely reliable, the test failing because the test area leaks so that the specified concentration of extinguishant cannot be maintained for an adequate time (Taylor, 1987). It follows that if greater attention is given to the integrity of the enclosure, performance requirements can be met without reliance on test procedures that cause the emission of environmentally unacceptable quantities of halon.

The industry position is that there are no environmentally acceptable alternatives that are as effective as halons and that they should continue in use whilst at the same time emissions can be significantly reduced (Taylor, 1987; HRI, 1988a). This could be achieved by the following measures (Andersen, 1987; Taylor, 1987).

²⁷ McFarlane, personal communication.

- Installation of halon fire control systems only where alternatives are inappropriate.
- Abolition of full-discharge tests using halons.
- Use of surrogates with zero or low ODP in test protocols.
- Improvement in modelling fire control system behaviour to reduce the frequency of tests.
- Increasing the maximum allowable halon concentration following discharge to provide more reliable fire protection whilst minimising the need for full discharge testing (coupled with further study on human toxicity and the development of improved warnings and alarms to prevent inhalation).
- Improvement and standardization of design of halon-protected space to minimise leakage during tests and to restrict halon release only to the compartment necessary (independent cellular protection).
- Improved ability to recover and recycle halons following discharge (accidental and test).
- Improvement of detectors to reduce accidental discharges.
- Establishing greater facility for human intervention to cancel halon release in the case of false alarms and greater control over manual releases of halons.
- Increasing the qualification requirements for halon system engineers and installers.
- More rigorous education and training for users and operators, including modified servicing standards and training with simulators.

The Canadian and U.S. governments are now committed to implementing the *Montreal Protocol* which calls for a freeze of halon production at 1986 levels by 1992. The *CEPA* is intended to support the Montreal agreement but is not bound by it and some non-essential uses of ozone-depleting substances will be banned, possibly halons (Buxton, 1988). The Canadian government, using Phase II of its *CEPA* legislation, and possibly even before this takes effect, intends to proceed with codes of practice that involve "recycle, recapture and reuse". Some substances will be prohibited completely unless it is judged that they conform to the category of "essential use" — applications for which there is an established need, with clear general benefits to society and for which there is no practical substitute (Buxton,

1988).

Use of Alternative Substances

Whilst alternatives may exist for testing systems (see above) the general opinion is that there are no replacements for halons that have desirable characteristics as extinguishants but which are environmentally safe, even at higher cost (HRI, 1988a). A recent report (BCR, 1988) claims success with a replacement for halon 1211 called NAF which gives rises to less-toxic fumes than halons and has an ODP ~ 1 and which is approximately one-third that of halon 1211. Even if this compound is effective, it is still composed of ozone-depleting chemicals and would probably only be considered as an interim replacement. Reliance on alternative compounds is, at best, a long-term solution (Taylor, 1987) and their development and deployment will take an estimated 5-10 y (HRI, 1988a). Clearly there is a considerable research effort in this direction but the information is of a commercial, proprietary nature²⁸. The industry position is that halons remain a viable option for fire protection for the present and in the immediate future (HRI, 1988a).

Disposal and Recycling

Their expense and use in closed systems led to an initial supposition that halons would be recycled minimising their potential environmental impact (Andersen, 1987) but rising atmospheric levels and the predictions from simulation models suggests that this has not been the case. There are no obvious technical obstacles to establishing a recycling programme which should be feasible from fixed halon systems.

Portable extinguishers are currently inspected and tested (presumably with considerable loss of halon) every six years. The industry is proposing to extend its "six-year teardown cycle" to 12 y because an adequate method of recovering and recycling the halon is not yet available (HRI, 1988a,b). Because the greater part of all halons that have been produced are currently banked (see above) the benefits of

²⁸ McFarlane, personal communication.

recycling would be considerable. Halons are expensive and contribute a large proportion to the cost of fire control systems (Taylor, 1987). This has been used to suggest that expense of the compound will encourage people to recover some costs through recycling on the decommissioning of systems. This would doubtless have advantages during a phase-down when a demand for halons would still exist but would not be feasible under a ban or phase-out, the discounted value of the halon would be minimal.

Disposal also presents an important opportunity to minimise the environmental impact of halons given the very large halon banks (Tables 3 & 5). For example, one major N. American corporation is considering decommissioning its (~1600) hand-held halon fire extinguishers and collecting them into two central locations (one each in the U.S. and Canada) pending the development of an environmentally safe disposal method. This is considered preferable to paying a waste disposal operation to remove them when there is no assurance that this has been done correctly²⁹.

Phase-Down versus Phase-Out

It is not usually feasible to institute an immediate ban on substances that, despite their harmful effects, confer benefits upon the community (e.g., fire protection in the case of halons) and for which there are no obvious immediate alternatives. A period during which substitutes can be developed and produced, operating systems modified and both producers and consumers permitted to adapt is required. Use of the substance may be curtailed (phase-down) or abolished (phase-out) or a progressive and incremental transition made between the two over appropriate time scales.

The options for regulating a phase-down/out include "permits, fees, command and control, labelling and voluntary reductions, and government leadership" (Andersen, 1987), the principal functions of each being summarised:

- *Permits*: issued to producers or users, possibly with the option of transferring them to other producers/users to ensure efficient allocation of production and consumption.

²⁹ FitzGerald, personal communication.

- *Regulatory Fees*: levied to increase costs of use and so encourage search for alternative strategies.
- *Control Technology*: optimal technology is specified to minimise emissions and some uses are proscribed if alternatives are available.
- *Labelling and Voluntary Control*: use of labels to assist users to avoid environmentally harmful substances and to encourage development of alternatives by industry.
- *Institutional Procurement Standards*: major institutions, especially governments, can provide leadership and influence the market place in favour of products that are more environmentally acceptable.

The U.S.A. was committed to a long-term, (10-20 y) phase-out (<95% of the then current emissions) of halons (Andersen, 1987). Under the 1985 *Vienna Convention on the Protection of the Ozone Layer*. In 1986 the EPA proposed halon 1301 and 1211 emissions be frozen at the (then) current levels followed by a long-term reduction in emissions with their deployment being tolerated only for essential uses, the scheme being finely tuned with respect to the time frame and inclusion/exclusion of other ozone depleting substances as appropriate to advances in knowledge. Canada made more stringent proposals in which emissions would be a function of population and Gross National Product (GNP). The wide spread acceptance of the 1987 *Montreal Protocol* has altered this situation, particularly with respect to U.S. Emissions.

To stabilise atmospheric bromine derived from halon emission, Hoffman & Gibbs (1988:3) argue that this will require a 100% phase-out of halon 1301 and a 90-100% phase-out of halon 1211 with 100% participation.

The provisions of the *CEPA* potentially go beyond those of the *Montreal Protocol* and the government of Canada may well exercise its option to establish extremely stringent standards for ozone-depleting chemicals, including halons (Buxton, 1987).

Conclusions

Halons are man-made compounds widely used as fire suppressants and specialised refrigerants. They are halogenated organic compounds, similar in many ways to CFCs except that they contain at least one bromine atom in the molecule. Their halogenation and lack of a hydrogen atom in the molecule makes them chemically stable, environmentally persistent and results in a long atmospheric residence time which enables them to reach the stratosphere. Halons breakdown in the stratosphere under the photolytic influence of UV radiation liberating active bromine Br_x which enters into many chemical reactions in a manner similar to active chlorine Cl_x . In comparison with chlorine, a much greater fraction of stratospheric bromine exists in the active form making halons potent destroyers of the ozone.

Source Data on Halons

Accurate assessment of the environmental impact of halons require reliable quantification of their production, banking and releases to the atmosphere. Because the concern over halons is relatively recent; they are proprietary compounds; they are subject to a complex international trade involving export and re-export the source data are currently less adequate than desired. Information from North America is reasonably reliable, that for Europe and Japan less so and information from the eastern bloc and developing countries almost non-existent. Information on the use and emission by the military is not generally available.

Production and Banks

Halon 1211 is primarily used in portable fire extinguishers. Current global production is $\sim 14,000 \text{ t y}^{-1}$ and the amount banked probably exceeds 17,000 tonne.

Halon 1301 is used in fire suppression of fixed installations and its use is growing in the computer and petrochemical industries. Current annual, global production probably exceeds 8,000 t and the global bank is judged to be large (e.g., the U.S. bank alone currently exceeds 25,000 t).

Halon 1301 is widely used by the military as fire control and fire suppressants in both aircraft and naval vessels. Most information on its use is either classified or otherwise not readily available. It would be useful in developing emissions scenarios to have some data on the military use of halons.

Sources of Emission

Global annual emissions of halon 1211 are probably $\sim 4,000 \text{ t y}^{-1}$. For both major halons only $\sim 25\%$ of the total emissions result from their discharge in fires control, the majority of releases occurring during production, accidents and other unwanted discharges, disposal and decommission of plant. Over half of the emissions result from releases during training exercises. Emissions of halon 1301 are probably in the range $1,000\text{-}2,000 \text{ t y}^{-1}$ with over 30% resulting from releases during tests of extinguishant systems.

Atmospheric Abundance

Halon 1211 undergoes only slight photolytic breakdown in the troposphere. Tropospheric abundances are $<2 \text{ pptv}$ falling off rapidly above the tropopause. Annual increases have been estimated to be in the range $10\text{-}30\%$ but a value of $\sim 12\%$ seems representative for most latitudes with an increase of $22 \pm 5\%$ reported from the Antarctic.

Current tropospheric abundances of halon 1301 are $\sim 1.5 \text{ pptv}$ and increasing at $4.0\text{-}4.5\%$ annually. This compound is more stable than halon 1211, undergoing almost no photolysis in the lower atmosphere and its abundance diminishes less rapidly with increasing altitude above the tropopause.

Ozone Depletion by Halons

The ODP of the halons (i.e., their ability to destroy ozone on release into the atmosphere relative to that of CFC-11 on a molecule for molecule basis) is much greater than most of the CFCs, being approximately 3 (halon 1211); 6 (halon 2402) and 11-12 (halon 1301). Because their atmospheric abundances are less than those of the CFCs, they are not the major current concern, for example halon 1211

currently accounts for ~2% of the ozone depletion resulting from man-made pollutants and bromine released from halons may currently be responsible for ~20% of the ozone loss over the Antarctic and adjacent southern latitudes. However, especially in the case of halon 1301, the long atmospheric lifetime (80-110 y) and high ODP (~11-12) suggests that they will become relatively more important in the future, especially as the search for replacements and proposals for recycling/destruction have received relatively little consideration compared with those for the CFCs.

Predictions of Future Halon Impacts

Both halon 1211 and 1301 are in widespread use and their use and emission to the atmosphere are increasing. Linear extrapolation suggests that by the year 2,000, the U.S production of each compound could reach ~12,000 t y⁻¹ and the U.S banks could approach 70,000 t. Using these figures as Source terms it is not surprising that some simulations have predicted extremely high surface abundances. However, a number of these numerical simulations were undertaken and published before the institution of the *Montreal Protocol* in 1987 and so do not consider that halon production may be pegged at the 1986 level by 1992. Two recent simulations that do consider the *MP* scenario nonetheless suggest that this cap on production will not be sufficient to reduce the ozone depleting effect of halons to acceptable levels (column abundance of halon 1211 could stabilise at 3-8 pptv; halon 1301 at 16-23 pptv).

Depending upon the scenario chosen, one simulation suggests that, even under the provision of the *MP*, anthropogenic pollutants could cause a 5-10% depletion of stratospheric ozone one-quarter to one-half of which could be attributed to halons.

The results of these studies should be critically appraised with respect to the underlying assumptions concerning the future production and emissions of halons that are used as source functions and the technical performance of the numerical simulation models used.

Managing the Halon Bank

The enormous stockpile of halons in fire control systems presents a significant management problem to the users (and technical problems to those who try to simulate future emissions to the atmosphere).

In response to the growing environmental concern and recognition of the fact that there are no immediate alternatives to halons, the producers and industrial associations appear to have moved quickly and responsibly to analyze the sources of emissions and make recommendations on how to reduce and eliminate unnecessary releases to the atmosphere. These measures include attention to operational protocols in the use of halons (specifically to minimise unnecessary use and losses *other* than those unavoidably incurred in fire protection.

It is not clear how widely such procedures have been and will be adopted. Major corporations in North America and Western Europe appear to be paying close attention to these issues in their management of halon 1301 systems. The existence of large numbers of portable 1211 fire extinguishers presents a more difficult problem. It is probable that the lead taken by the industry will have to be supplemented by legislation covering both operating and testing procedures. The desirable measures of reuse and recycling and ultimately the destruction of halons, will probably also require legislation. The destruction of the halon bank is not an option before replacement compounds are available.

It is not known if military operating protocols have been changed to reduce unwanted emissions matching civilian procedures.

Alternatives, Phase-Down, Phase-Out

There is only one possible halon replacement currently under development and information on this is limited. Alternatives are probably not going to be available for about a decade necessitating a phase-down leading to a total abolition of halons when substitutes are available. Various schemes have been proposed under the *Vienna Convention* and the *MP* but the time scales appear to be at variance with the needs for environmental protection. The *CEPA* goes beyond the provision of the *MP* but further simulation is needed to assess how adequate such measures would be if

they were universally adopted.

Computer Simulation Models

Numerical simulation of chemical, physical and dynamical processes in the atmosphere is essential for assessing the impacts of halons. Whilst the principal limitation on simulation studies is the reliability of the estimates of production and future emissions, particularly the fate of the halon bank, the simulation methods themselves bear closer scrutiny.

Sensitivity Analysis

Further simulation studies should give attention to the sensitivity of the model outputs to changes in the source terms and parameterizations and would benefit greatly from a clearer exposition of the strengths and limitations of the algorithms and choice of source terms, variables and parameterizations used. The one-dimensional models employed do not adequately describe many of the processes (e.g., downward and lateral transport) that conceivably affect the fate of halons in the atmosphere. Again, discussion of these limitations is usually lacking.

Several published simulations report reasonable agreement between simulated and observed atmospheric abundances. In the absence of sensitivity studies, and given that abundances are often close to the detection limit of the analytical instruments used, it is not clear how much of this agreement is fortuitous.

Scenarios

The fate of the bank is crucial to assessing the environmental impact of halons. An extended series of simulations that address the fate of the halon bank in realistic terms is needed. For example, the consequences of: (i) not recycling the halon bank; (ii) partially recycling the halon bank; (iii) completely recycling the halon bank; (iv) effect of changes in the proportions of halons 1211, 1301 and 2402 production and emissions. Simulations should also consider halon contributions to climate warming.

Greenhouse Impacts

Halons have potential for contributing to a climatic warming although estimated future abundances suggest that increases in surface temperature will not be significant ($<0.1^{\circ}\text{C}$). The potential greenhouse impacts should continue to be considered in appraisals of how much and how fast halons are going to increase in atmospheric abundance.

Halon 2402

Clearly a better quantification of halon 2402 production, use and emission is needed. Although relatively little is produced at present, its use appears to be increasing and it has an ODP of ~ 6 which is between that of halons 1211 and 1301. Given that this is a strategic chemical such information may not be forthcoming.

International Ordinances

At present the only ordinances that prescribe reductions in halon production are those under the provisions of the *MP* and it appears that these are not sufficiently stringent to ameliorate the anticipated environmental impacts. Clearly the various national and international initiatives directed at minimising ozone depletion and greenhouse warming that have followed on from the Montreal initiative should consider how tighter controls can be legislated.

So far such ordinances appear to address only the issues of halon production; the fate of the halon bank is at least, if not more important than production and requires similar attention by the appropriate agencies.

The Atmospheric Research Agenda

The need for better estimation of the use and release of halons to the atmosphere coupled with more comprehensive numerical simulation of their fate should be complemented by improvements in the detection and monitoring of persistent brominated compounds in the atmosphere and studies on the chemistry of Br_x and its participation in ozone destroying catalytic reactions with other halogens.

Halons and the Canadian Environmental Protection Act (CEPA)

With respect to the *CEPA*, halons are *toxic or capable of becoming toxic* within the context of the act, namely that they have *an immediate or long-term harmful effect on the environment* and cause or potentially cause *a danger to the environment on which human life depends*. It follows that it may be prudent to consider including halons on the *Priority Substances List* under the Act.

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Appendices

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A2 The Halons

Halon 1211

Chemical Names & Formula bromochlorodifluoromethane
chlorodifluoromonobromomethane, CBrClF_2

Trade Names & Synonyms halon 1211, halocarbon 12B1, freon-12B1

Physical Data

Molecular Weight	165.37
Boiling Point	-3.8°C @ 760 mm Hg
Freezing Point	-160°C
Melting Point	-160.5°C
Vapour Pressure	1773 kPa @ 20°C
Vapour Density	5.7 @ 20°C
Specific Gravity	1.83 @ 4°C
Aqueous Solubility	very low
Taste & Odour	colourless gas at normal temperature and pressure, slightly sweet odour

Ozone Depletion Potential (ODP) 2.4-2.7

Reactivity etc.

Inflammable but high temperatures and presence of some metals (magnesium and its alloy with >2% Mg in presence of water, potassium, sodium, aluminum, zinc, natural rubber, metallic hydrides) may promote catalytic decomposition.

Thermal decomposition produces HCl, HBr, HF and/or toxic fumes of chlorides, bromides and fluorides.

Toxicity & Medical Treatment

Vapour almost non-harmful unless inhaled. Liquid causes chilling/freezing of tissue on contact. Frostbite if swallowed or extensive and/or prolonged contact with skin and cornea.

Prolonged contact with skin can lead to the cutaneous absorption of significant and harmful quantities.

Asphyxiation if inhaled (exposure to >4% v/v for >1 min causes vertigo, nausea, vomiting, disorientation, confusion and narcosis) leading to suffocation at high concentrations.

No evidence of chronic toxicity from repeated exposure.

For skin contact, wash thoroughly with soap and water, if irritation persists or freezing obvious treat as for frostbite by bathing/showering with warm ($<105^{\circ}\text{F}$) water and seek a physician. For eye contact, flush with water >20 -15 min and seek physician/ophthalmologist.

For inhalation, remove to fresh air and apply artificial respiration for apnoea and oxygen from dyspnoea and seek physician.

Adrenalin is contraindicated because fluorocarbons sensitize the myocardium, treatment to be directed at control of symptoms and clinical conditions.

Selectively abstracted from the *Canadian Centre for Occupational Health and Safety* database supplied by industry and other sources. The original sources should be consulted with respect to caveats concerning the accuracy and currency of this information and for full details on use, handling, spill treatment, disposal, emergency clean-up and medical treatment.

Halon 1301

Chemical Name & Formula bromotrifluoromethane, CBrF_3

Trade Names & Synonyms halon 1301, freon-1381

Physical Data

Molecular Weight	149
Boiling Point	-58°C @ 101.3 kPa (abs)
Freezing Point (triple)	-168°C @ 101.3 kPa (abs)
Vapour Pressure	1166 kPa @ 15°C
Liquid Density	1992 kg m ⁻³ @ -58°C & 101.3 kPa (abs)
Gas Density	m ⁻³ @ 15°C & 101.3 kPa (abs)
Specific Gravity	5.21 @ 15°C & 101.3 kPa (abs)
Aqueous Solubility	0.005 v/v @ 25°C & 101.3 kPa with low hydrolysis
Taste & Odour	slight odour of ether

Ozone Depletion Potential (ODP) ~11.4

Reactivity etc.

Incompatible with alloys containing >2% magnesium in presence of water.

Toxic products result when mixtures with flammable gases are ignited.

Toxicity & Emergency Medical Treatment

Relatively non-toxic but in high concentrations causes asphyxiation by the displacement of oxygen in air. Victim should be removed to uncontaminated area and given artificial respiration and a physician summoned if necessary.

Toxic products result when mixtures with flammable gases are ignited.

Selectively abstracted from the *Canadian Centre for Occupational Health and Safety* database supplied by industry and other sources. The original sources should be consulted with respect to caveats concerning the accuracy and currency of this information and for full details on use, handling, spill treatment, disposal, emergency clean-up and medical treatment.

in various studies it was found that the use of the following formulae for the calculation of the various parameters of the system is not very accurate. The following formulae are more accurate and should be used for the calculation of the various parameters of the system.

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Halon 2402

Chemical Name & Formula	dibromotetrafluoroethane, $C_2F_4Br_2$
Trade Names & Synonyms	halon 2402, fluobrene, freon 114B2

Physical Data

Molecular Weight	259.83
Boiling Point	47.3°C
Freezing Point	-110.5°C
Vapour Pressure	6.6 @ 122°C, 16.5 @ 120°F
Liquid Density	790 kg m ⁻³ @ 214.5°C @ 500 psi abs
Taste & Odour	slightly sweet taste/odour
Appearance	clear, colourless liquid

Reactivity etc.

Thermal decomposition at 400°C yielding gaseous HBr and HF detected by irritation at levels below those considered dangerous.

Ozone Depletion Potential (ODP) ~6

Toxicity & Emergency Medical Treatment

Relatively toxic to humans at exposures below those required to extinguish fires. Its use is proscribed for indoor areas normally under human occupation in many countries.

Concentrations of 13% v/v considered fatal although a fatality occurred at ~3% v/v. Maximum acceptable human exposure is 0.05% v/v (500 ppm) for 10 min; 0.10% v/v (1,000 ppm) for 1 minute.

Halon 2402 causes extreme myocardial sensitization to catecholamines (adrenaline, noradrenaline, epinephrine, norepinephrine) and the administration of (for example) adrenaline is contraindicated in cases of collapse and cardiac arrest.

Selectively abstracted from a variety of sources which should be consulted with respect to caveats concerning the accuracy and currency of this information and for full details on use, handling, spill treatment, disposal, emergency clean-up and medical treatment.

Chemical Name & Formula: 2,4-Dichlorophenoxyacetic acid (2,4-D)
 Trade Name & Supplier: 2,4-D, 2,4-Dichlorophenoxyacetic acid (2,4-D)

Physical Data

Molecular Weight	201.03
Boiling Point	273°C
Melting Point	115°C
Vapor Pressure	0.001 mm Hg at 25°C
Density (water)	1.48 g/cm ³ at 25°C
Water Solubility	0.001 g/l at 25°C
Log P (octanol/water)	4.74

Reactivity

The acid is a weak acid, with a pK_a of 2.8. It is a weak base, with a pK_b of 11.2. It is a weak oxidizing agent, with a redox potential of 1.1 V.

Chemical Reactions

Reaction with Alcohols

Reaction with alcohols is a common reaction for 2,4-D. It is a weak acid, with a pK_a of 2.8. It is a weak base, with a pK_b of 11.2. It is a weak oxidizing agent, with a redox potential of 1.1 V.

Concentration of 2,4-D in water is 0.001 g/l at 25°C. The concentration of 2,4-D in water is 0.001 g/l at 25°C. The concentration of 2,4-D in water is 0.001 g/l at 25°C.

Reaction with alcohols is a common reaction for 2,4-D. It is a weak acid, with a pK_a of 2.8. It is a weak base, with a pK_b of 11.2. It is a weak oxidizing agent, with a redox potential of 1.1 V.

Reaction with alcohols is a common reaction for 2,4-D. It is a weak acid, with a pK_a of 2.8. It is a weak base, with a pK_b of 11.2. It is a weak oxidizing agent, with a redox potential of 1.1 V.

A3 Abbreviations, Acronyms, Chemical Formulae & Glossary

absorption cross section

Ratio of the (electromagnetic) energy removed by a target (atom, molecule, radical etc.) to that incident upon it.

abundance (atmospheric)

Quantity of a substance present in a unit of the atmosphere, for traces gases usually expressed in pptv or ppbv.

AES

Atmospheric Environment Service, Environment Canada.

alkanobromine

Hydrocarbon of the paraffin series (e.g., methane, ethane, propane, etc.) in which one or more hydrogen atoms is replaced by the halogen bromine.

allotrope

One of two or more distinct physical forms in which a pure element may exist (e.g., the di- and triatomic forms of oxygen).

bank (halon)

The accumulating quantity of halon stored, or banked, in fire control and other systems. This greatly exceeds annual production and is central to a consideration of future emissions scenarios.

Br

bromine

BrO

bromine

BrO_x

General symbol for species of bromine oxides.

bromine	Chemical element of Group 7A, the halogens Present in natural compounds and in man-made substances including halons, it participates in a number of ozone-destroying reactions in the stratosphere.
bromine monoxide	An important intermediary in the ozone depleting chemical cycles in the stratosphere, reacting with (another) BrO or ClO to liberate free Br.
bromochlorodifluoromethane	halon 1211
bromoform	Naturally occurring organobromine compound, CHBr ₃ .
bromotrifluoromethane	see halon-1301
carbon dioxide	CO ₂ , a natural component of the carbon cycle and greenhouse gas whose atmospheric abundance has increased greatly this century as a result of the human use of fossil fuels.
CF ₂ BrCl	halon 1211
CEPA	Canadian Environmental Protection Act
CF ₃ Br	halon 1301
C ₂ FBr ₂	halon 2402
CFC-11 & CFC-12	The principal chlorofluorocarbon (freon) refrigerants responsible for the depletion of the ozone layer through their liberation of Cl _x in the stratosphere.
CFC	chlorofluorocarbons
CFM	chlorofluoromethane

chlorine

Chemical element of Group 7A, the halogens. Present in a number of natural compounds in the atmosphere and in the man-made CFCs and halons 1211, it participates in a number of ozone-destroying reactions in the stratosphere.

chlorine dioxide

ClO₂, its accumulation is an important diagnostic indicator of ozone depletion in the Antarctic.

chlorine monoxide

ClO, important in that it participates in the ozone depleting chemical cycle of the stratosphere, reacting with another ClO or with BrO to liberate free Cl.

chlorine nitrate

ClONO₂, formed if NO_x is abundant in the stratosphere when it reduces the availability of active Cl_x.

chlorodifluoromono-bromomethane

halon 1211

chlorofluoromethane

Man-made halocarbon containing one carbon atom and at least one fluorine and one chlorine atom.

Cl

atomic chlorine

Cl₂

The normal, gaseous diatomic allotrope of chlorine.

Cl_x

chlorine species

ClO

chlorine monoxide

ClO_x

chlorine oxide species

Cl₂O₂

chlorine dioxide

ClONO₂

chlorine nitrate

CO₂

carbon dioxide

concentration

see mixing ratio

holding time	Maintenance of required concentration of extinguishant (usually halon 1301) for a specified period during a test of a fixed fire control system.
DSS	Department of Supply & Services, Can.
EDF	Environmental Defense Fund
emission (atmospheric)	The release of a compound into the atmosphere.
endothermic (reaction)	Chemical reaction releasing energy in the form of heat.
EPA	Environmental Protection Agency, U.S.A.
ethylene dibromide	$C_2H_2Br_2$, an alkanobromine emitted to the atmosphere by natural processes and human activity.
FEMA	Fire Equipment Manufacturers Association, U.S.
FSSA	Fire Suppression Systems Association, U.S.
FOE	Friends of the Earth
formaldehyde	H_2CO , an important atmospheric hydrocarbon derived from natural sources and human activity.
freon-1381	halon 1301
greenhouse (gas, effect etc.)	Heating of the planet's surface and atmosphere by the absorption and re-emission infrared radiation by and from the atmosphere. This is a natural phenomenon responsible for the maintenance of the normal global temperature. It is argued that the warming has been enhanced by the excess atmospheric accumulation of trace <i>greenhouse</i> (or RAGs) gases which increase the radiative transfer to

	the earth's surface. These gases are emitted by human perturbation of natural biogeochemical cycles and the release of man-made chemicals to the atmosphere. The functional analogy to a greenhouse is incorrect.
H	atomic hydrogen
HBr	hydrogen bromide
halocarbon	Hydrocarbon molecule in which one or more hydrogen atoms has been replaced by one or more halogen elements (includes the CFCs and halons).
halogen	Elements of Group 7A of the periodic table comprising fluorine, chlorine, bromine, iodine, and astatine. They are highly reactive and substitute for hydrogen in many organic compounds (halocarbons). Chlorine and bromine are particularly implicated in the destruction of stratospheric ozone by man-made halocarbons.
halon	Halocarbons used in fire control and containing at least one bromine atom in the molecule (see halon 1211, 1301 & 2402). They have large ODPs, liberating Br in the stratosphere and although their atmospheric abundance is much less than that of the CFCs it is increasing.
H ₂ CO	formaldehyde
HFEASC	Halon Fire Extinguishing Agent Statistical Committee, U.S.
hν	solar photon
HRI	Halon Research Institute, U.S.
hydrogen bromide	HBr, emitted to the atmosphere by natural processes and human activity.

hydroperoxyl radical	HO ₂
hydroxyl radical	OH
ICI	Imperial Chemical Industries Ltd.
infrared (radiation)	Electromagnetic radiation λ 0.75/0.8-10,000 μm . See also longwave.
°K	degree(s) kelvin
km	kilometre
lifetime (atmospheric)	Literally the residence time of a compound in the atmosphere but usually expressed as an <i>e-folding lifetime</i> in numerical computations where the abundance of the substance declines by 1/e or to ~37% of the initial value after one lifetime.
longwave (radiation)	That part of the infrared electromagnetic spectrum emitted by the earth and its atmosphere in the temperature range 200-300°K and $\lambda > 4\text{-}100 \mu\text{m}$.
LTS	List of Toxic Substances, under the <i>CEPA</i> .
M	Reactant carrying away energy from chemical reaction.
m	metre
methyl bromide	CH ₃ Br
min	minute (time)
mixing ratio	Measure of atmospheric concentration, usually the ratio of a mass of a gaseous substance to that of the mass of dry air.

Montreal Protocol

°N

NAF

NAFED

NAS

NASA

NFPA

NFPRF

nitrogen dioxide

nitrous oxide

NFPA

NGO

nm

NO₂

N₂O

NO_x

An international protocol, widely adopted in principle at Montreal, Canada in 1987, but not yet universally ratified by the signatories, intended to effect controls over CFC and halon production. Under the *MP* production of all three halons would be fixed at the 1986 levels by 1992.

degree(s) latitude north

Proprietary compound comprising 50% CFC-11, 20% CFC-12, 15% CFC-114 and the balance in edible oils under trial as possible substitute for halon 1211.

National Association of Fire Equipment Distributors, U.S.

National Academy of Sciences, U.S.

National Aeronautics and Space Administration, U.S.

National Fire Protection Association, U.S.

Fire Protection Research Foundation, U.S.

NO₂

N₂O

National Fire Protection Association, U.S.

Non-Governmental Organisations

nanometre, 1×10^{-9} m

nitrogen dioxide

nitrous oxide

nitrogen oxide species

O	oxygen
O ₂	The stable diatomic allotrope of gaseous oxygen.
O ₃	ozone
OC10	chlorine dioxide
ODE	Ozone Depletion Efficiency (synonymous with ODP).
ODP	Ozone Depletion Potential
OH	hydroxyl radical
ozone	The triatomic and relatively unstable allotrope of oxygen. Ozone is formed in the stratosphere and absorbs solar radiation strongly in the UV (0.1-0.3 μm, 0.4-0.65 μm) and infrared (4.7, 9.6 & 14.1 μm) bands. In absorbing the UV it acts as the primary heat source of the atmosphere and shields the earth's surface from this biologically harmful part of the spectrum
Ozone Depletion Potential	The ability of a compound to cause the dissociation of ozone relative to that of CFC-11 & 12 which have ODPs approximating (by definition) unity. The index is a function of the atmospheric lifetimes and molecular weights of the compound relative to that of the CFCs and the number and identity of the halogen species in the molecule. The ODP expresses the comparative depletion potential on a molar basis: the ultimate threat posed by a compound being a function of its ODP <i>and</i> abundance.

ozone hole

A dramatic but imprecise description of the major (~50%) depletion of stratospheric ozone first reported over Antarctica in the austral spring of 1985. The result of both dynamical and chemical processes, it is now clear that Cl and Br released by man-made chemicals play a major role in the loss of ozone. The depletion principally is confined by the polar vortex but extends to the high mid-latitudes. Heterogenous phase chemical reactions taking place on the surface of ice crystals that form the PSCs are important and the depletion is greater in years of low stratospheric temperature. A parallel phenomenon occurs in the Arctic but the chemical and dynamical factors appear to differ in many ways from those taking place in the S. hemisphere.

ozone layer

That region of the stratosphere at altitude 10-50 km characterised by a high concentration of ozone. Ozone, which is most concentrated at 20-25 km, is formed by photodissociation of diatomic oxygen under the influence of solar UV radiation. The ozone layer plays an important role in the radiative balance of the planet and its atmosphere and protects the biota from excessive, harmful UV radiation.

ozone (total column
or amount)

This total, called the *column ozone amount* or the *total ozone*, is usually specified as the thickness of a layer of pure ozone at standard temperature and pressure (STP) which would contain the same number of ozone molecules. The total ozone varies daily, seasonally and geographically between extreme values of 2 mm and 6 mm, with a current global average over the earth's surface of approximately 3.5 millimetres.

photodissociation

Chemical decomposition caused by the breaking of chemical bonds by photons.

POD

Potential Ozone Depleter

Polar Stratospheric Clouds

Clouds of ice crystals formed in the stratosphere at temperatures below -80°C . The crystals provide surfaces on which a variety of heterogeneous phase chemical reactions, important in the depletion of stratospheric ozone over the poles, may take place.

Potential Ozone Depleters

Compounds whose chemical structure suggests that they may facilitate the breakdown of stratospheric ozone although there may be no direct evidence that they have done so.

ppbv

Parts per billion by volume, one part in 10^9 by volume.

pptv

Parts per trillion by volume, one part in 10^{12} by volume.

PSC

Polar Stratospheric Cloud

PSL

Priority Substances List under the *CEPA*.

Radiatively Active Gas(s)

Synonym for *greenhouse* gases whose absorption of particular wavelengths of the electromagnetic spectrum leads to an enhancement of the so-called *greenhouse effect*, leading to a possible climate warming. These include man-made compounds such as CFCs and halons.

RAGs

Radiatively Active Gas(s)

SF_6

see sulphur hexafluoride

shortwave (radiation)	Solar radiation with a peak intensity at $\sim 0.5 \mu\text{m}$ and confined within the limits $\lambda 0.29 < 4.0 \mu\text{m}$ (see ultra violet radiation).
sink	Location in, or process by, which a substance is removed from a system.
stratosphere	The atmosphere between $\sim 10/15$ to 50 km where temperature increases with height and is controlled by the radiation balance.
sulphur hexafluoride	Chemical formula SF_6 , compound used as a surrogate for halon 1301 in testing fire control installations
t	metric tonne, 10^3 kg
tropopause	The atmospheric boundary between the troposphere and stratosphere usually characterized by an abrupt change in the lapse rate. The altitude varies, being 15-20 km in tropics and 10 km in polar regions.
troposphere	The lower layer of the atmosphere in which most clouds and precipitation are confined. It extends from the surface to 10-20 km and characterized by a general decrease in temperature with altitude.
ultraviolet radiation	Electromagnetic radiation of wavelength in the range 1-400 nm ($0.001\text{-}0.4 \mu\text{m}$) which may be divided into UV-A (315-400 nm), UV-B (280-315 nm) and UV-C (100-280 nm).
μm	micrometre, $1 \times 10^{-6} \text{ m}$
UV	See ultraviolet radiation
UV-B	See ultraviolet radiation
Vienna Convention	<i>Vienna Convention on the Protection of the Ozone Layer</i>

WMO

World Meteorological Organisation of
the U.N.

y

year

A4 Tables

Table 1. Index Transformation Results of A4 Elements
Since 1970

Year	Index 1970		Index 1975	
	production	in thousands	production	in thousands
1970	1970		1970	
1971	1.141	1×10^3	1.147	1×10^3
1972	1.241	1×10^3	1.243	1×10^3
1973	1.270	1×10^3	1.270	1×10^3
1974	1.271	1×10^3	1.286	1×10^3
1975	1.270	1×10^3	1.286	1×10^3
1976	1.270	1×10^3	1.286	1×10^3
1977	1.271	1×10^3	1.287	1×10^3
1978	1.270	1×10^3	1.279	1×10^3
1979	1.270	1×10^3	1.279	1×10^3

Figures in parentheses for 1970, 1975, and 1979 are
in units of 1000 of 1970 production and are
rounded to 3 figures.

*Table 1. Halon Production, Europe & N.America
Since 1978.*

Year	Halon 1301 production t (% increase)	Halon 1211 production t (% increase)
1978	2,823	6,487
1979	3,241 (+14.8)	6,292 (-3.0)
1980	3,841 (+18.5)	6,641 (+5.5)
1981	4,760 (+23.9)	6,419 (-3.3)
1982	5,674 (+19.2)	7,396 (+15.2)
1983	5,380 (-5.2)	7,284 (-1.5)
1984	5,759 (+7.0)	8,700 (+19.4)
1985	6,031 (+4.7)	10,437 (+20.0)
1986	6,940 (+15.0)	11,792 (+13.0)
1987	7,690 (+10.8)	13,588 (+15.2)

Figures presented by J.G.Hartley, ICI Industries
in June 1988 at Lugano, Switzerland and made
available by G.Taylor.

Table 2. Halon Use and Emissions in 1985

Emissions	Halon 1301	Halon 1211
<i>t (% total emissions)</i>		
1986 U.S. load ¹	3,500	2,750
total emissions ² ,	1,002(29.3)	430 (16.3)
entering new equipt.	2,475(70.8)	2,309(80.4)
<i>t (% total load)</i>		
total emissions	1,002(29.3)	430 (16.3)
<i>t (% total load, % total emissions)</i>		
manufacture, R&D, shipping etc.	90(2.6, 8.9)	40(1.5, 9.1)
fill-related	93 (2.7, 9.3)	
discharge test	311 (8.9, 31.0)	31(1.1, 7.2)
fires	234 (6.7, 23.4)	114 (4.1, 26.5)
unwanted discharge	199 (5.7, 19.9)	31 (1.1, 7.2)
service & leakage	93 (2.7, 9.3)	
training	5 (both ≤ 1.0)	225 (8.2, 52.3)

1. load [annual] = domestic production + imports) - exports by manufacturers and distributors. 2. emissions approx. equal losses for all categories except for use in fires where ~10% assumed to be converted into non ozone-depleting substances. Recalculated from data presented in *Industrial Economics*, 1987 collected in 1986 from major trade organizations and published by Andersen (1987).

Table 3. U.S. Bank and Emissions of Halon 1211 in Tonne

Year	Demand*	Bank	Additions to Bank*	Emissions	Weighted Emissions**
1970	57	0	55	1	4
1971	57	55	53	4	9
1972	57	108	51	6	15
1973	136	159	126	10	25
1974	136	286	121	15	37
1975	273	407	249	23	58
1976	318	656	283	34	86
1977	455	938	404	49	123
1978	569	1,342	499	69	171
1979	713	1,841	618	92	231
1980	893	2,460	768	122	304
1981	1,118	3,227	955	158	396
1982	1,400	4,183	1,191	204	510
1983	1,753	5,373	1,485	261	653
1984	2,196	6,859	1,855	332	830
1985	2,750	8,713	2,309	430	1,074
1986	3,102	11,011	2,540	547	1,369
1987	3,501	13,551	2,794	690	1,725
1988	3,944	16,345	3,073	849	2,123
1989	4,434	19,419	3,381	1,028	2,569
1990	4,992	22,799	3,719	1,244	3,109
1991	5,466	26,518	4,016	1,415	3,538
1992	5,978	30,534	4,338	1,601	4,002
1993	6,606	34,872	4,685	1,876	4,690
1994	7,201	39,557	5,059	2,090	5,225
1995	7,972	44,616	5,464	2,450	6,125
1996	8,705	50,080	5,901	2,738	6,845
1997	9,577	55,982	6,373	3,131	7,827
1998	10,485	62,355	6,883	3,520	8,801
1999	11,481	69,238	7,434	3,957	9,893
2000	12,578	76,672	8,029	4,449	11,123

* Historical US demand is based on industry estimates for the years 1970 to 1985. Demand from 1986 to 2000 is based on growth rates in additions to the bank of 10 percent for 1985–1990 and 8 percent for 1990–2000.

** Weighted Emissions = Emissions × 2.5.

Source: *Industrial Economics*, 1987.

Information submitted to the U.S. EPA, June 1987 with the cooperation of the fire equipment industry (taken from Andersen, 1987).

Table 4. Atmospheric Lifetime, Estimated Emissions and Ozone Depletion Halons 1211 & 1301

Halon	Atmospheric Lifetime (y)	Estimated 1985 Emissions (10^3 t)	Relative O ₃ Depletion	Share Total O ₃ Depletion (%)
1301	100.9	3	11.4	3.7
1211	12.5	3	2.7	0.9

Adapted from Hammitt *et al.* (1988: Table 1).

Table 5. U.S. Bank and Emissions of Halon 1301 in Tonne

Year	Demand*	Bank	Additions to Bank*	Emissions	Weighted Emissions**
1965	23	0	21	2	20
1966	26	21	23	3	31
1967	29	44	26	4	43
1968	33	70	28	5	55
1969	72	98	63	9	100
1970	111	161	97	14	158
1971	149	258	130	20	229
1972	188	387	161	27	311
1973	227	548	192	35	406
1974	409	740	353	56	639
1975	591	1,094	510	81	932
1976	773	1,603	661	112	1,283
1977	1,273	2,264	1,101	172	1,974
1978	1,136	3,365	940	196	2,258
1979	1,474	4,305	1,221	253	2,906
1980	1,812	5,525	1,493	318	3,659
1981	2,149	7,018	1,724	424	4,877
1982	2,487	8,742	1,958	528	6,072
1983	2,825	10,700	2,142	681	7,836
1984	3,162	12,841	2,331	830	9,542
1985	3,500	15,172	2,475	1,023	11,766
1986	3,798	17,647	2,598	1,197	13,763
1987	4,293	20,245	2,728	1,562	17,961
1988	5,083	22,973	2,865	2,215	25,475
1989	5,939	25,838	3,008	2,927	33,661
1990	6,569	28,845	3,158	3,407	39,178
1991	7,093	32,004	3,316	3,772	43,375
1992	7,719	35,320	3,482	4,232	48,664
1993	8,166	38,802	3,656	4,504	51,796
1994	8,671	42,458	3,839	4,826	55,499
1995	9,199	46,297	4,031	5,161	59,350
1996	9,749	50,327	4,232	5,509	63,358
1997	10,325	54,560	4,444	5,872	67,533
1998	10,926	59,004	4,666	6,251	71,883
1999	11,700	63,670	4,899	6,791	78,093
2000	12,498	68,569	5,144	7,343	84,444

* US demand is based on industry estimates for the years 1970 to 1985. Demand from 1985 to 2000 is based on a 5 percent average annual growth rate in additions to the bank over that period.

** Weighted Emissions = Emissions $\times$ 11.5.

Source: *Industrial Economics*, 1987.

Information submitted to the U.S. EPA, June 1987 with the cooperation of the fire equipment industry (taken from Andersen, 1987).

Table 6. Annual Increase Halon Abundance

Halon	Percentage	Reference
1211	10 - 30	Khalil & Rasmussen (1985c), Lal <i>et al.</i> (1985)
	22 ± 5	Khalil & Rasmussen (1985c) cited WMO (1985:75)
	20	Lal <i>et al.</i> (1985)
	12 - 13	Singh <i>et al.</i> (1988:595)
1301	4.0-4.5	Singh <i>et al.</i> (1988:595)

Table 7. Atmospheric Halons

Halon	Measured Conc. (pptv)	Year	Est. Global Indust. Prod'n. ($\times 10^6$ kg)	Ref.	Est. Atm. Lifetime (year) ^a
1301	~1.0	1976	1.4-3.0	b	110.0
	1.3 ^e	1984	7.0-8.0	c,d	
1211	~1.2 2.2-3.6 ^f	1984	(~5.0?) ^e	c	25.0

a. NAS (1984), b. WMO (1985:73), c. DuPont, personal communication to authors of WMO, (1985), d. Khalil & Rasmussen (1985a), e. release estimated from observed atmospheric abundances, uncertain delay between industrial production and release to the atmosphere, f. calculated from increases in atmospheric abundance, Singh *et al.* (1988:595). Abstracted from WMO (1985:70).

Table 8. Atmospheric Concentrations of Halons

Halon	Year	Conc. (pptv)	Lat.	Reference
1301		0.7		Penkett <i>et al.</i> (1981)
		~0.06-0.9 ^a		Fabian <i>et al.</i> (1981a)
	1984	1.0	90 S	Khalil & Rasmussen (1985c)
	1987	0.12-1.24 ^b	17 N	Singh <i>et al.</i> (1988)
	1987	0.05-1.28 ^c	44 N	Singh <i>et al.</i> (1988)
1211	1978	0.16		Lovelock,
	1980	0.43	~51 N	cited
	1981	1.45		WMO (1985)
	1981	1.09 ± 0.10 ^d	72 N	Rasmussen & Khalil (1984c)
	1982	1.03	72 N	Lal <i>et al.</i> (1985)
	1983	1.31	72 N	Lal <i>et al.</i> (1985)
	1983	0.9-1.2 ^e	72 N	Rasmussen & Khalil (1984c)
	1984	1.10	90 S	Khalil & Rasmussen (1985c)
	1984	0.03-1.49 ^f	72 N	Lal <i>et al.</i> (1985)
	1985	2.00	44 N	Lal <i>et al.</i> (1985)
	1987	0.08-1.96 ^g	17 N	Singh <i>et al.</i> (1988)
	1987	0.06-1.96 ^h	44 N	Singh <i>et al.</i> (1988)

a. decreasing from approximately 10-26 km (interpolated from Fig.1), b. decreasing from approximately 11-29 km, c. decreasing from approximately 10-27 km (see Table 5), d. standard deviation, e. range, cited from WMO (1985:68), f. decreasing from tropopause to 23 km, g. decreasing from approximately 11-24 km (see Table 6), h. decreasing from approximately 10-21 km (see Table 6).

Table 9. Mean Volume Mixing Ratios (VMR) In Parts Per Trillion (pptv, 10^{-12}) Of Halon 1211 Over Latitudes 17 N And 44 N In 1987.

17 N		44 N	
Alt (km)	VMR (pptv)	Alt (km)	VMR (pptv)
11.44	1.96	10.11	1.96
13.91	2.04	14.20	1.76
15.57	1.93	17.21	0.84
17.29	1.87	18.95	0.64
19.37	1.44	21.20	0.06
21.22	0.73	21.60	0.06
23.42	0.11		
23.87	0.08		

Abstracted from Singh *et al.* (1988:594), see graphical plot Figure 3. Values of VMR were obtained by gas chromatography-electron capture detection.

Table 10. Halon Lifetimes And Conversion Factors

Compound	Lifetimes γ (% remaining) ^a			Conversion Factor ^b
	$\times 1$ (37%)	$\times 3$ (5%)	$\times 5$ (~1%)	
halon 1211	12.9	39	60	3.31×10^{-2}
halon 1301	100	303	465	3.68×10^{-2}

a. The lifetimes indicate how long the chlorine associated with the halons remain in the atmosphere. These are *e-folding* lifetimes from which it follows that after one lifetime $1/e$ or 37% of the original amount remains, the values for 3 and 5 lifetimes being 5% and ~1% respectively. b. The conversion factors convert millions of kg halon emitted into atmospheric abundance in pptv for each compound. Modified from Connell (1986) cited by Hoffman & Gibbs (1988, Exhibit 2).

Table 11. Estimates of the Quantity of Halons in the Atmosphere Years 1980-2030

Halon	Source	Sink	Est. Ave Res.Time (years)	Global Average Mix. Ratio (pptv)	Projected Global Ave Conc. (pptv)		References
					Probable Value	Possible Range	
1301	anthropo- genic	strat.	110.0	1.0 (1980) ~1.0 (1988)	5.0 (2030) 13.0 (2075)	3.0-100.0	Ramanathan <i>et al.</i> (1985) Hoffman & Gibbs (1988)
1211	anthropo- genic	trop. < strat.	25.0	~1.0 (1988)	6.0 (2075)		Hoffman & Gibbs (1988)

Abstracted from various sources.

Table 12. Halons 1211 and 1301 production, emission and surface abundance for a *quartile* of the score function for years 1985, 2000 and 2040 for various scenarios

Year	Item	0.05	0.25	0.50	0.75	0.95	Scenarios 1 & 2	
Halon 1301								
1985	production	10.7	10.7	10.7	10.7	10.7		
	emissions	3.0	3.0	3.0	3.0	3.0		
	abundance	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2000	production	13.6	16.7	19.4	22.4	27.7		
	emissions	5.6	6.5	7.1	7.9	9.2		
	abundance	4.99	5.43	5.75	6.13	6.73	5.75	3.39
2040	production	9.9	24.2	43.2	75.4	163.0		
	emissions	8.5	14.7	22.0	33.6	62.9		
	abundance	22.8	31.8	40.6	52.9	80.6	40.6	0.3
Halon 1211								
1985	production	10.7	10.7	10.7	10.7	10.7		
	emissions	3.0	3.0	3.0	3.0	3.0		
	abundance	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2000	production	13.6	16.7	19.4	22.4	27.7		
	emissions	5.6	6.5	7.1	7.9	9.2		
	abundance	3.23	3.55	3.78	4.06	4.50	3.78	2.10
2040	production	17.5	34.1	55.1	89.6	182.0		
	emissions	16.1	24.6	33.9	47.9	81.3		
	abundance	14.9	19.8	24.8	31.8	468.0	24.9	3.15

SCENARIO 1, Cap on CFC-11 and CFC-12 emissions at 1985 levels, $p = 0.50$. *SCENARIO 2* zero emissions growth. Production and Emissions ($\times 10^3$ t), Surface Abundance (pptv $\equiv$ mole halon *per* mole atmosphere $\equiv$ mixing ratio). The *score function* defines the probability of that value being exceeded e.g., at a level of 0.75, the 2000 halon 1301 emissions are 7.9×10^3 t so that there is only a 0.25 (25%) probability that the actual emissions will be greater than this value. Combined from Tables 4&5 in Hammitt *et al.* (1987).

Table 13. Mean Volume Mixing Ratios (VMR) In Parts Per Trillion (pptv, 10^{-12}) Of Halon 1301 Over Latitudes 17 N And 44 N In 1987

17 N		44 N	
Alt (km)	VMR (pptv)	Alt (km)	VMR (pptv)
11.44	1.24	10.11	1.28
13.91	1.35	14.20	1.14
15.57	1.22	17.21	0.70
17.29	1.20	18.95	0.45
19.37	1.01	21.20	0.33
21.22	0.74	21.60	0.26
23.42	0.43	22.60	0.19
23.87	0.42	23.75	0.19
24.88	0.30	24.85	0.19
25.55	0.25	25.85	0.13
26.61	0.29	27.10	0.05
29.00	0.12		

Abstracted from Singh *et al.* (1988:594), see graphical plot Figure 9. Values of VMR are means of simultaneous measurements by gas chromatography-mass spectrometry and gas chromatography-electron capture detection.

Table 14. Absorption Features of Halon 1301

Approx. Spectral Range (cm ⁻¹)	Band Intensity (cm ⁻¹ (atm cm) ⁻¹ 296K)	Reference
1060-1110	1908	Pugh & Narahari Rao (1976)
1180-1240	1914	

Abstracted from WMO (1985:831).

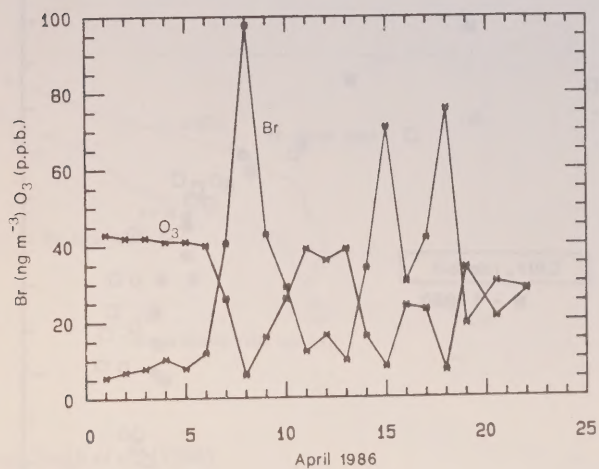
A5 Figures

Figure 1. A line graph showing the relationship between the concentration of a substance (Y-axis) and time (X-axis). The graph illustrates a sharp increase in concentration followed by a gradual decrease, with a small peak around the middle of the time period.



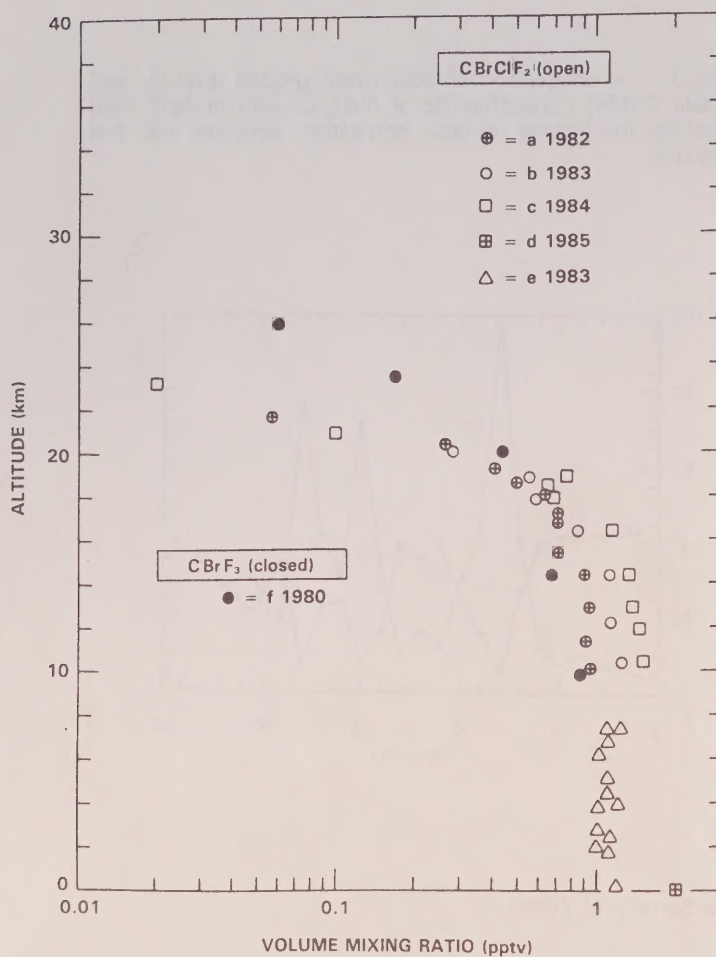
Figure 1. A line graph showing the relationship between the concentration of a substance (Y-axis) and time (X-axis). The graph illustrates a sharp increase in concentration followed by a gradual decrease, with a small peak around the middle of the time period.

Figure 1. A comparison of daily mean ground level O_3 and filterable Br(f-Br) concentrations at Alert, Canada in April 1986 illustrating the strong inverse correlation between the two parameters



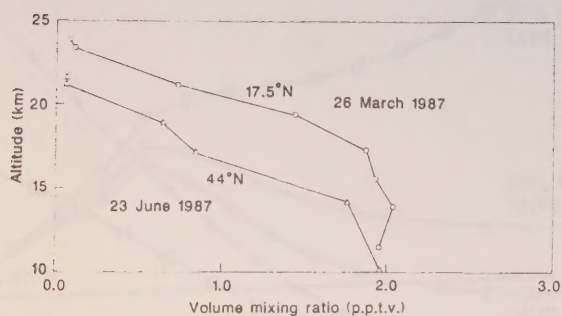
From Barrie *et al.* (1988).

Figure 2. Vertical Distribution of CBrClF_2 (FC-121) and CBrF_3 (F-13B1) at Northern Midlatitudes.



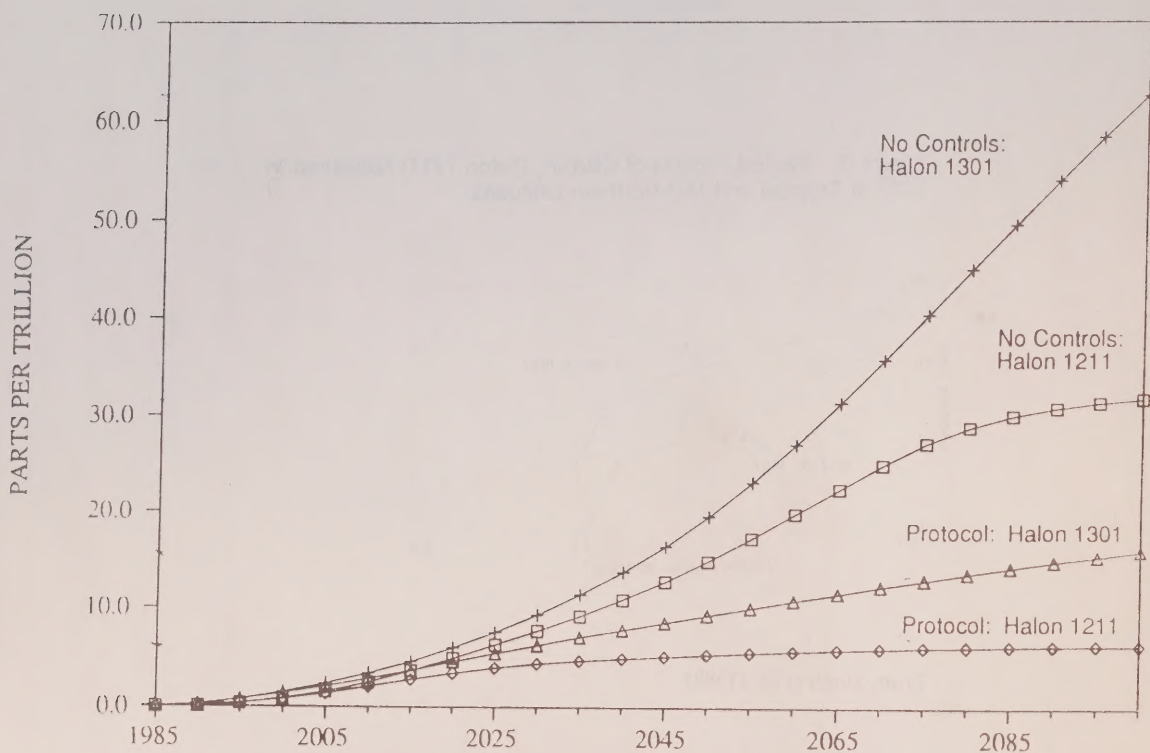
a-d. Lal *et al.* (1985); e. Rasmussen & Khalil (1983b); f. Fabian *et al.* 1981a). From WMO (1985: 639, Vol. II).

Figure 3. Vertical Profiles of CBrClF_2 (halon 1211) Measured in 1987 at Tropical and Mid-Northern Latitudes.



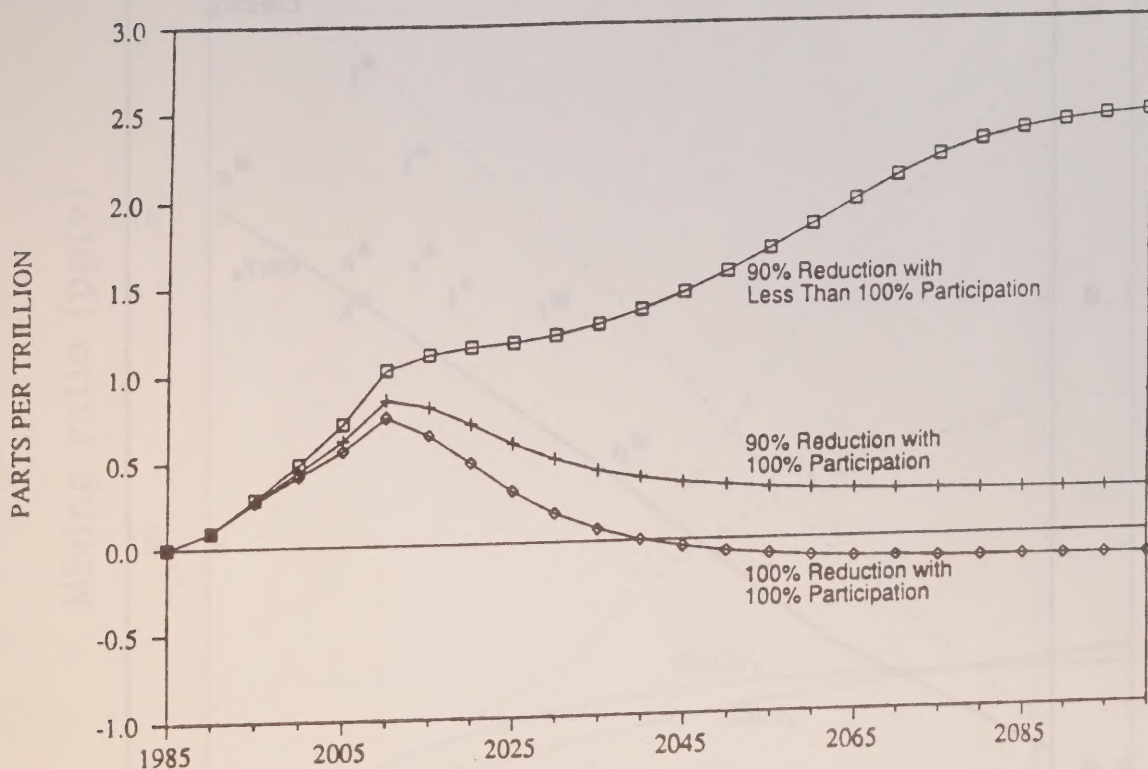
From Singh *et al.* (1988).

Figure 4. Simulated Increase in Halon Levels: No Controls and Protocol Scenarios.



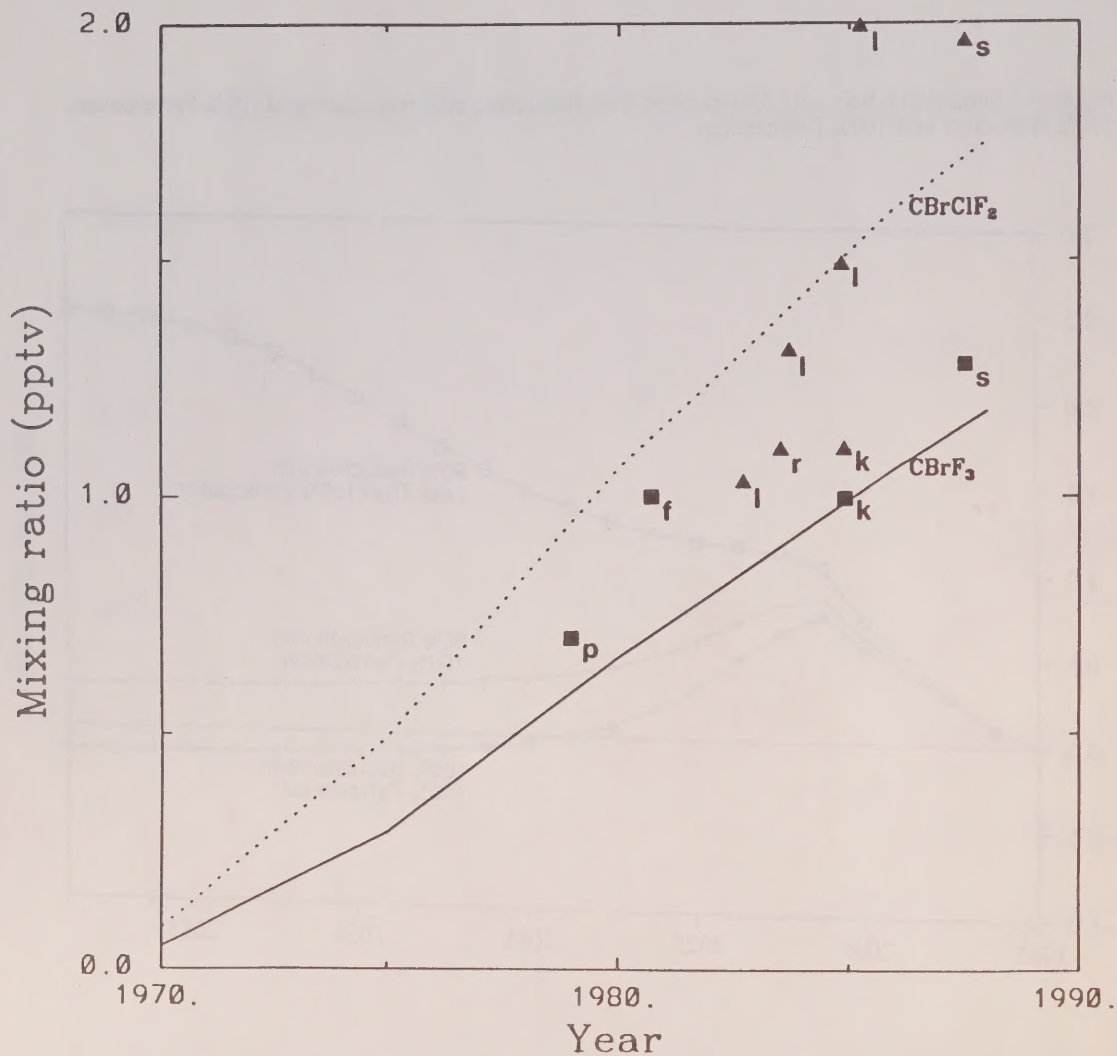
Assumptions. ♦ Protocol participation: U.S. participation; 94% of other developed nations; 65% of developing nations. ♦ Baseline compound use is assumed to be constant after 2050. From Hoffman & Gibbs (1988).

Figure 5. Simulated Halon 1211 Abundances: 90% Reduction; 90% Reduction and 100% Participation; 100% Reduction and 100% Participation.



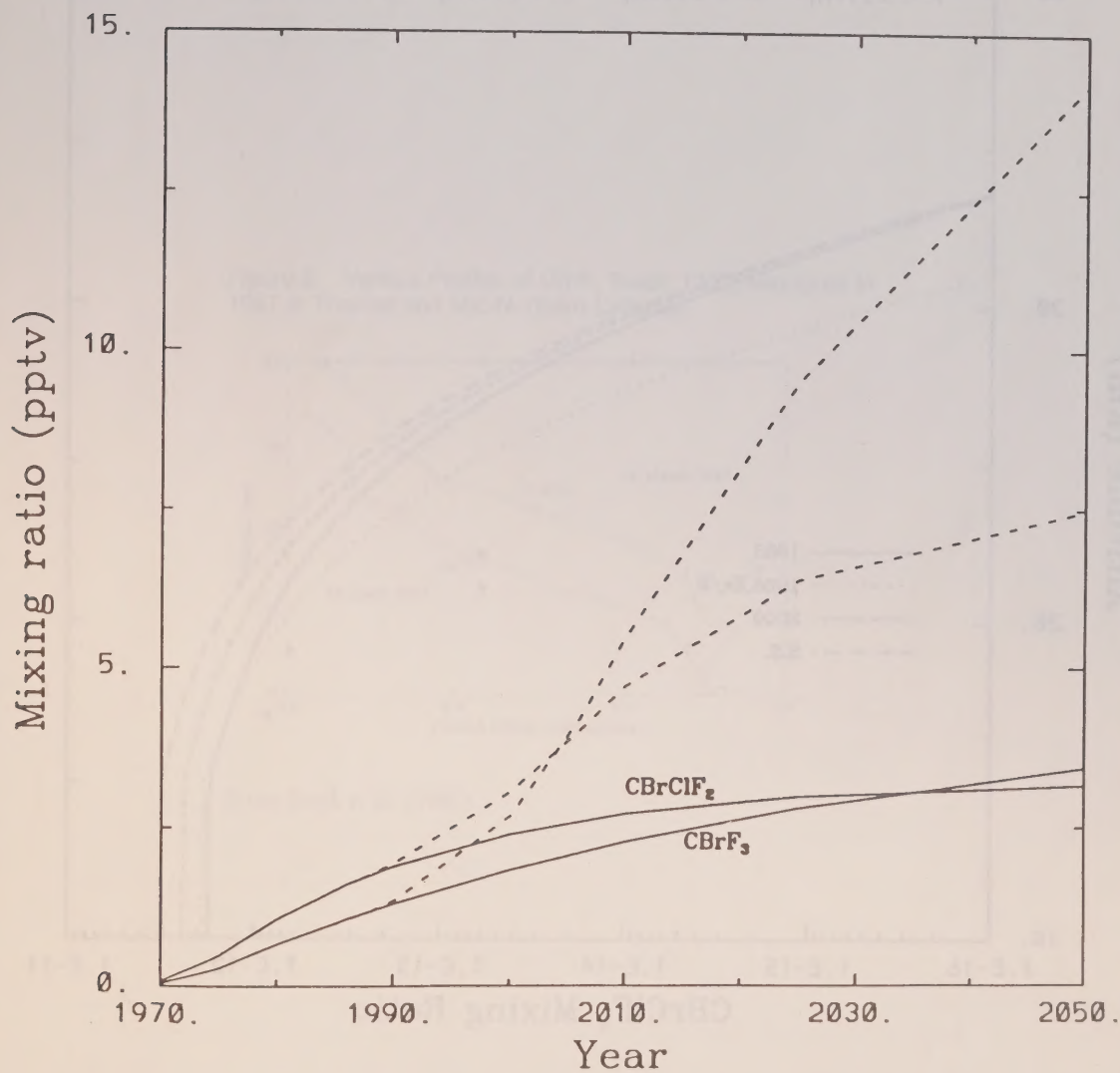
Halon 1211 is assumed to be released slowly over 30 years after it is placed in fire extinguishers. Most of the emissions occur within the first 20 years after charging. Baseline compound use is assumed to be constant after 2050. From Hoffman & Gibbs (1988: 54).

Figure 6. Concentration (pptv) versus time (y) plots for CBrClF_2 (halon 1211) and CBrF_3 (halon 1301) up to 1988.



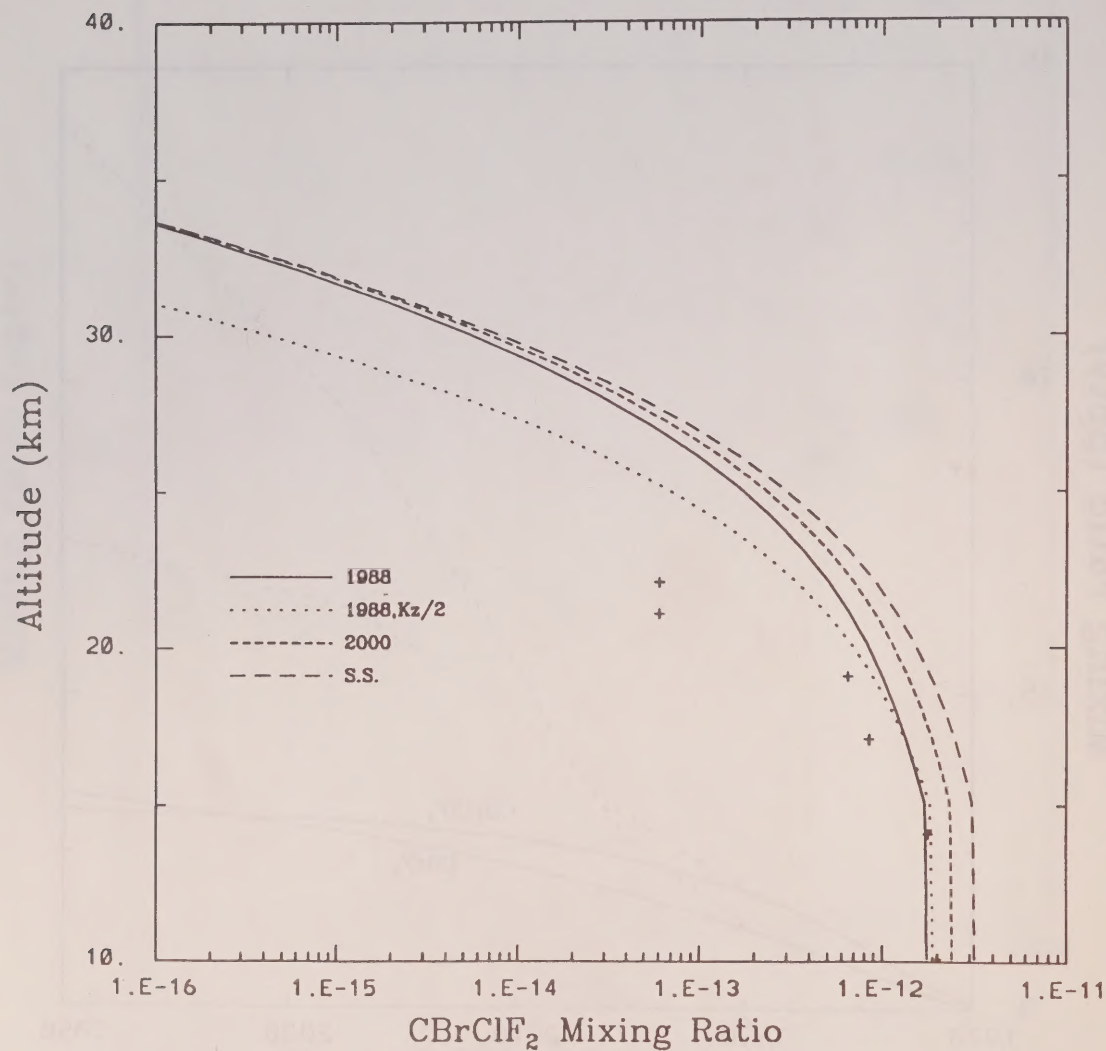
CBrClF_2 measurements: Δ_L Lal *et al.* (1985) 44°N at 10 km; Δ_K Khalil & Rasmussen (1986); Δ_S Singh *et al.* (1988) 44°N at 10 km; Δ_R Rasmussen & Khalil (1984) for Jan-Dec in the Arctic. CBrF_3 measurements: $\square_P$ Penkett *et al.* (1981) at surface; $\square_F$ Fabian *et al.* (1981) 44°N at 10 km; $\square_K$ Khalil & Rasmussen (1986); $\square_S$ Singh *et al.* (1988) 44°N at 10 km. After McConnell *et al.* (1989).

Figure 7. Concentration (pptv) versus time (y) plots for CBrClF_2 (halon 1211) and CBrF_3 (halon 1301) up to 2050.



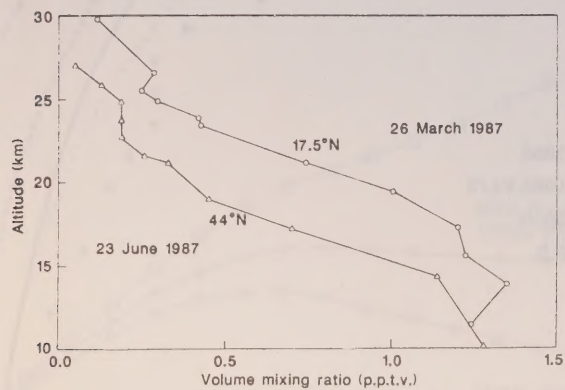
Data as for Figure 7. Dashed curves are for scenario BB. After McConnell *et al.* (1989).

Figure 8. Concentration (pptv) versus altitude (km) profiles for CBrClF_2 (halon 1211).



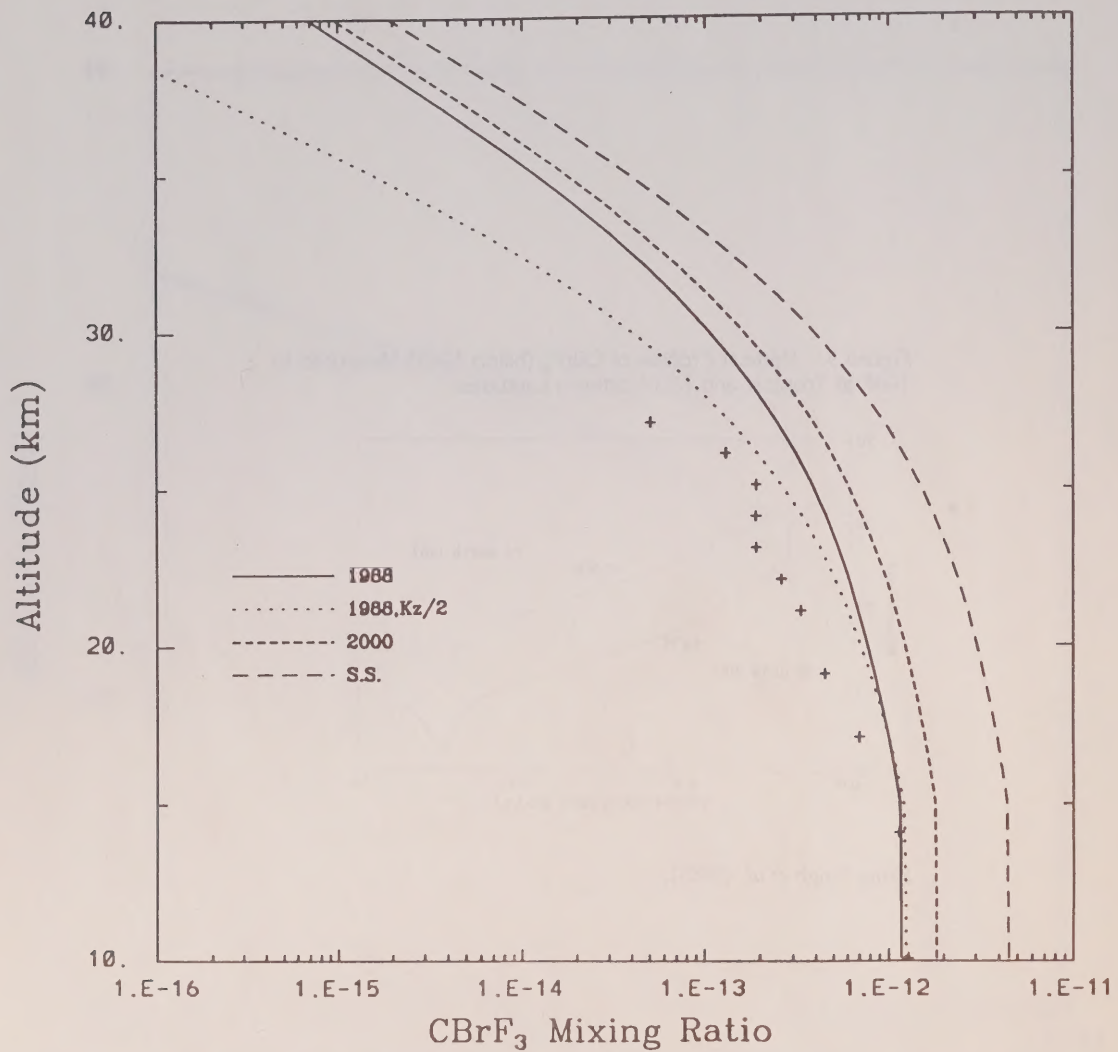
Model curves for years 1988, 2000 and at steady state are shown along with measured data from Singh *et al.* (1988). also shown are steady state model results for $0.5K_z$. After McConnell *et al.* (1989).

Figure 9. Vertical Profiles of CBrF_3 (halon 1301) Measured in 1987 at Tropical and Mid-Northern Latitudes.



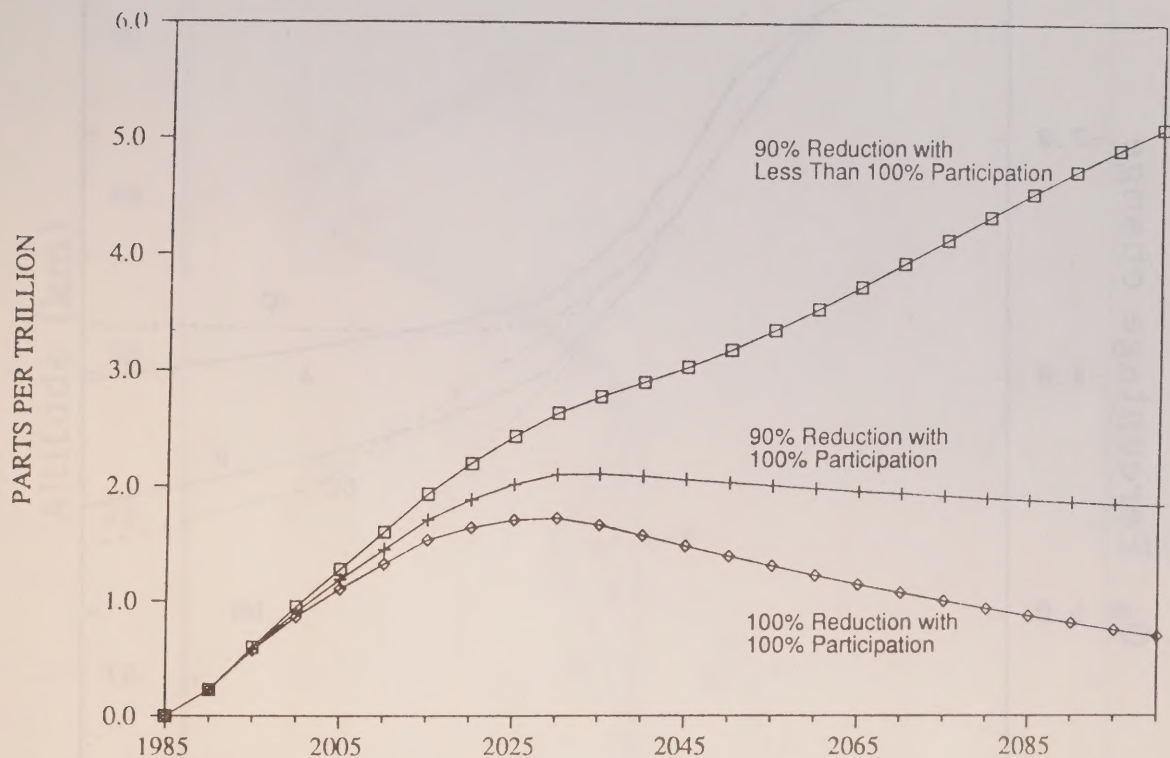
From Singh *et al.* (1988).

Figure 10. Concentration (pptv) versus altitude (km) profiles for CBrF_3 (halon 1301).



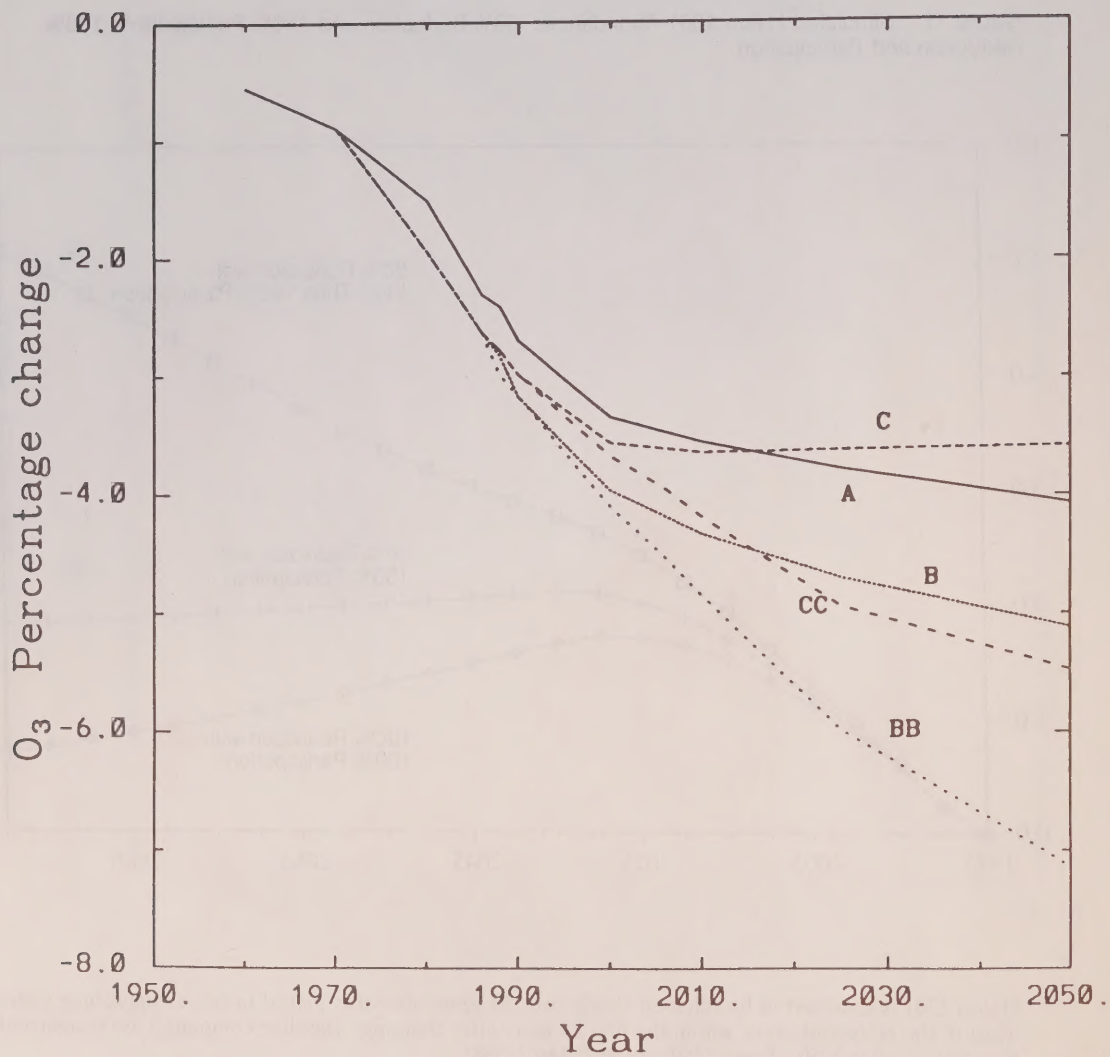
Model curves for years 1988, 2000 and at steady state are shown along with measured data from Singh *et al.* (1988). also shown are steady state model results for $0.5K_z$. After McConnell *et al.* (1989).

Figure 11. Simulated Halon 1301 Abundances: 90% Reduction and 100% Participation; 100% Reduction and Participation



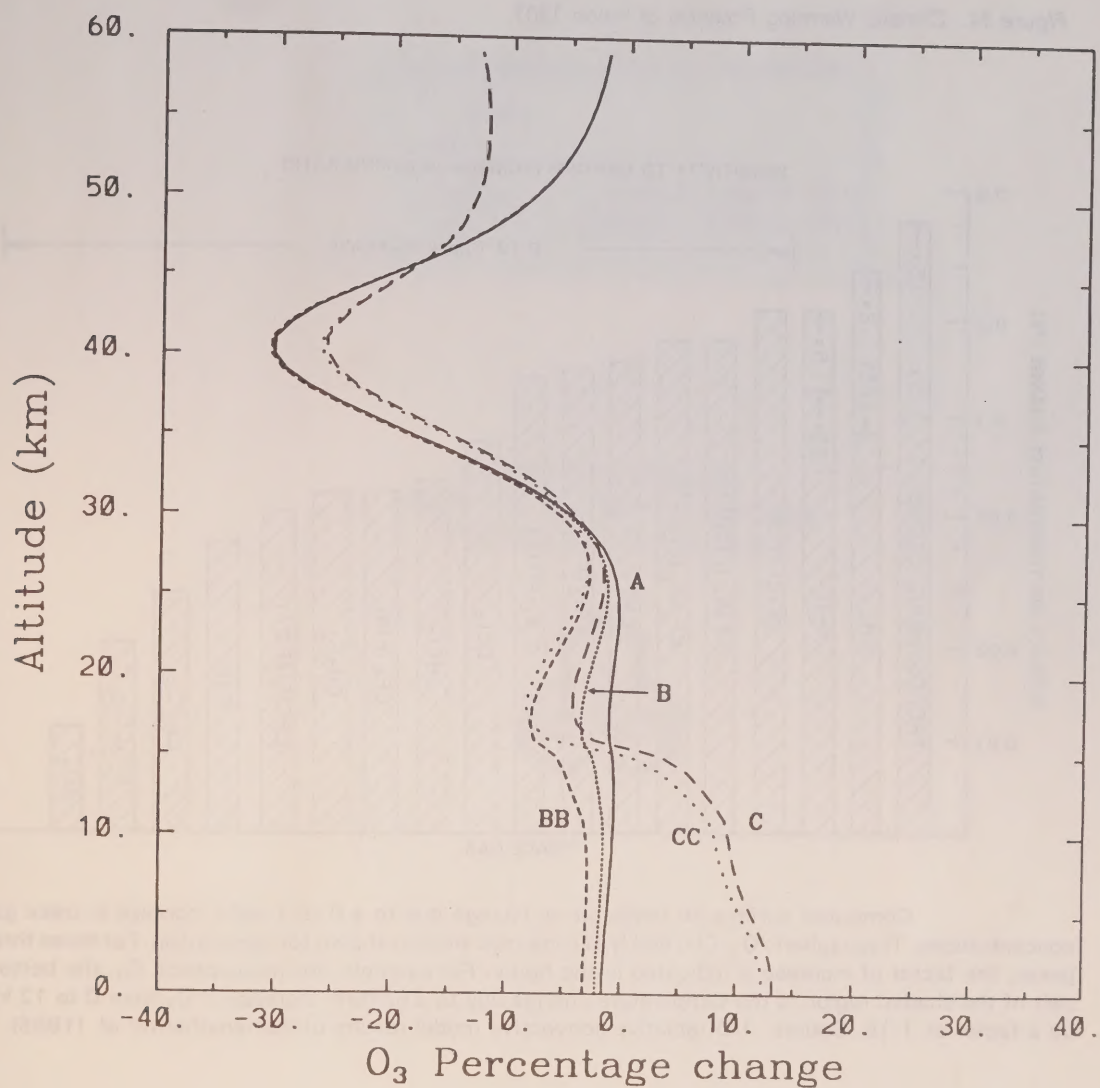
Halon 1301 is assumed to be released slowly over 40 years after it is placed in fire extinguishing systems. Most of the emissions occur within the first 25 years after charging. Baseline compound use is assumed to be constant after 2050. From Hoffman & Gibbs (1988).

Figure 12. Column Depletions of Ozone (%) Versus Time (years).



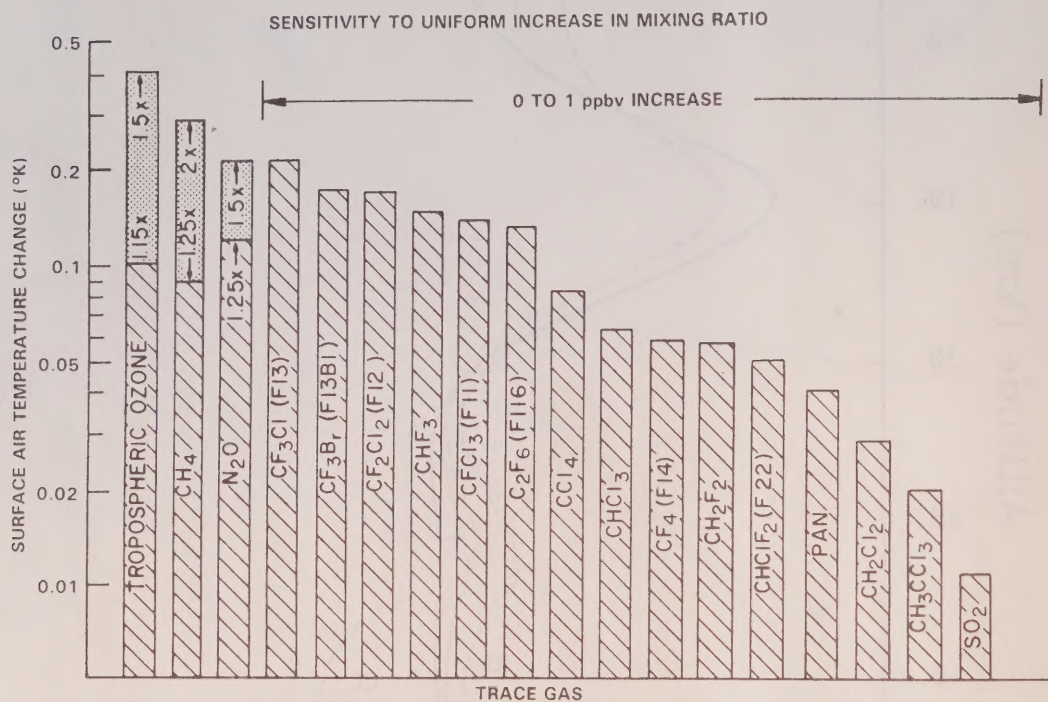
Calculated for each scenario described in the text. After McConnell *et al.* (1989).

Figure 13. Depletions of Ozone (%) Versus Altitude (km).



Calculated for each scenario described in the text. Profiles are given for the year 2050.
After McConnell *et al.* (1989).

Figure 14. Climatic Warming Potential of Halon 1301.



Computed surface air temperature change due to a 0 to 1 ppbv increase in trace gas concentrations. Tropospheric O₃, CH₄ and N₂O increases are also shown for comparison. For these three gases, the factor of increase is indicated in the figure. For example, for tropospheric O₃, the bottom part of the shaded region is the temperature change due to a uniform increase in O₃ from 0 to 12 km by a factor of 1.15. Source: 1-D radiative-convective model results of Ramanathan *et al.* (1985).

After WMO (1985).

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